# VIII. *The Constitution of the Alloys of Aluminium and Zinc.*

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*Communicated by* R. T. GLAZEBROOK, *C.B., F.R.S.*

Received January 30,—Read February 16, 1911.

[PLATES 5–7.]

THE alloys of aluminium and zinc have been studied as regards their constitution by HEYCOCK and NEVILLE,* SHEPHERD,† and EWEN and TURNER.‡ The present authors having occasion to study these alloys from the point of view of their mechanical and physical properties in a research carried out under the auspices of The Alloys Research Committee of the Institution of Mechanical Engineers, began by accepting the equilibrium diagram in which SHEPHERD had expressed the results of his investigation. A few cooling-curves, however, which were taken in the first place with the object of confirming SHEPHERD's results, immediately showed that the constitution of these alloys must be much more complex than had been supposed by SHEPHERD. It therefore seemed desirable to carry out a more complete investigation on the constitution of these alloys, and the results of that investigation are presented in the present paper.§

The materials used in the present investigation were: aluminium of a high degree of purity, kindly presented by the British Aluminium Company, and a very pure

* HEYCOCK and NEVILLE, "The Freezing-Points of Alloys containing Zinc and another Metal," 'Journ. Chem. Soc.,' vol. 71, 1897, p. 389.

† SHEPHERD, "Aluminium-Zinc Alloys," 'Journal of Physical Chemistry,' 1905, 9, p. 504.

‡ EWEN and TURNER, "Shrinkage of the Antimony-Lead Alloys," 'Institute of Metals,' September, 1910.

§ A brief preliminary account of some of the results of the present investigation has been given in the 'Annual Report of the National Physical Laboratory for 1909' (published March, 1910), and in a lecture by W. ROSENHAIN at the Royal Institution in June, 1910.

variety of zinc, kindly presented by Sir JOHN BRUNNER. The analyses of these materials are as follows :—

Aluminium—

| | |
|---|---|
| Silicon . . . . . | 0·17 per cent. |
| Iron . . . . . | 0·20 ,, |
| Copper . . . . . | Trace. |
| Aluminium (diff.) . . . . . | 99·63 per cent. |

Zinc—

The zinc used contained traces only of iron and silicon, and was of at least 99·98 per cent. purity.

The alloys were prepared by melting together weighed quantities of the two metals in salamander crucibles heated in a small furnace.

For the preparation of the alloys rich in aluminium, that metal was first melted and the requisite quantity of pure zinc added to it, the zinc dissolving very rapidly

TABLE I.—Calculated and Analytically Determined Composition of the Alloys.

| Alloy. | Calculated. | | Determined. | |
|---|---|---|---|---|
| | Zinc. | Aluminium. | Zinc. | Aluminium. |
| | per cent. | per cent. | per cent. | per cent. |
| 99 | 99 | 1 | — | 1·22 |
| 98 | 98 | 2 | — | 2·11 |
| 95 | 95 | 5 | 95·76 | — |
| 92 | 92 | 8 | 91·54 | — |
| 90B | 90 | 10 | 89·85 | — |
| 90 | 90 | 10 | 88·75 | — |
| 86 | 86 | 14 | 85·52 | — |
| 85 | 85 | 15 | 84·23 | — |
| 84 | 84 | 16 | 83·50 | — |
| 80 | 80 | 20 | 79·54 | — |
| 78 | 78 | 22 | 78·48 | — |
| 76 | 76 | 24 | 75·29 | — |
| 75 | 75 | 25 | 74·50 | — |
| 70 | 70 | 30 | 69·88 | — |
| 65 | 65 | 35 | 66·71 | — |
| 60 | 60 | 40 | 60·27 | — |
| 55 | 55 | 45 | 55·57 | — |
| 50 | 50 | 50 | 50·52 | — |
| 45 | 45 | 55 | 46·40 | — |
| 40 | 40 | 60 | 39·13 | — |
| 35 | 35 | 65 | 33·21 | — |
| 30 | 30 | 70 | 29·37 | — |
| 20 | 20 | 80 | 20·54 | — |
| 15 | 15 | 85 | 15·50 | — |
| 10 | 10 | 90 | 10·64 | — |
| 5 | 5 | 95 | 5·46 | — |

in the molten aluminium; in the case of alloys near the zinc end of the series a previously prepared alloy of equal parts of aluminium and zinc was usually melted first and further zinc subsequently added. All the ingots upon which the results stated in the paper are based have been chemically analysed, and the results obtained are shown in Table I., p. 316. In the majority of cases it will be seen that the analytically determined composition agrees very closely with that aimed at; in a few cases where discrepancies of over 1 per cent. are found this is due to repeated melting of the ingots in question.

During their preparation and subsequent treatment the alloys were carefully protected from contamination with foreign materials. The extent to which this was attained is illustrated in Table II., where the analyses of two alloys are given together with their composition (as regards impurities) as calculated from the materials used.

TABLE II.

| Alloy. | Impurities. | | | |
|---|---|---|---|---|
| | Calculated. | | Determined. | |
| | Iron. | Silicon. | Iron. | Silicon. |
| | per cent. | per cent. | per cent. | per cent. |
| 90B | 0·020 | 0·017 | 0·03 | 0·02 |
| 50 | 0·100 | 0·085 | 0·09 | 0·10 |

In most of the experiments the melting-furnace was heated by gas, but in other experiments a small electric resistance-furnace was employed.

Oxidation of the metals was minimised by keeping the temperatures of the melting-furnaces as low as possible consistent with the complete fusion of the alloys; it was not found practicable to protect the surface of the alloys by a flux, or other covering, without risking contamination from substances liable to be reduced by the molten aluminium.

The thermal study of the alloys was carried out by means of a series of cooling-curves taken by the "inverse-rate" method with the delicate potentiometer installed for that purpose at the Laboratory. The ingots used for obtaining these cooling-curves weighed 300 gr. and were cooled in a furnace which was placed in a closed water-jacketed steel vessel, the thermo-couple being introduced into the alloys through suitable apertures in the top of the water-jacket. The cooling alloys were thus entirely protected from draughts or other extraneous disturbances.

In a first series of cooling-curves the rate of cooling was such that when the alloys

were hot the temperature fell at a rate of 1° C. per second, the rate of cooling decreasing as the alloys cooled, until it became 1° C. in 12 seconds. It was found that this rate of cooling was too rapid and for the data used in the present paper a series of curves were obtained at much slower rates of cooling, ranging from a rate of fall of temperature of 1° C. in 4 seconds when the alloys were hot (near 650° C.) to a rate of 1° C. in 20 seconds when the alloys were cool (near 200° C.).

This slow rate of cooling was adopted because it was found that certain of the reactions or inversions which occur in these alloys are to a considerable extent suppressed by the more rapid rates of cooling; even the rate adopted does not allow these reactions to be completed, but they occur to a sufficient extent to allow unmistakable signs of their existence to appear on the cooling-curves. For the purpose of studying the alloys under conditions of *complete* equilibrium, it was, therefore, necessary to adopt the method of microscopic examination of samples which had been subjected to prolonged heating.

As already indicated, the temperature measurements were made by means of a thermo-couple and potentiometer. One thermo-couple, composed of wires of platinum and platinum with 10 per cent. of iridium, has been used throughout the research; this junction has never been broken or repaired, and it has been carefully protected from injury by such causes as unnecessarily high temperatures or contact with furnace gases or other injurious substances. At the beginning of the research, and frequently during its progress, this thermo-couple has been calibrated by using it to determine the freezing-points of a series of standard pure metals. In these calibrations the thermo-couple was used in the same small furnace, and with the same fire-clay protectors, as were employed in taking the cooling-curves, and similar rates of cooling were used. The temperature-E.M.F. curves obtained from these calibrations could therefore be applied direct to the readings of the cooling-curves without the introduction of any corrections. At the conclusion of the research the thermo-couple gave readings which agreed with the original calibration within 1° C.

The use of very slow cooling, and the fact that the alloys were allowed to solidify in a perfectly undisturbed manner, would seem to involve the risk that the observations might be vitiated by errors due to surfusion. Surfusion phenomena can, however, be detected readily with the apparatus used in this work, by the occurrence of a *rise* of temperature following the first arrest of cooling; although small rises of temperature of this nature were frequently observed, the large mass of alloy used, and the slow rate of cooling, always resulted in a prolonged arrest at a definite maximum temperature, and the manner in which the observed points fall upon smooth curves or upon straight lines shows that errors from surfusion have been avoided.

In the study of the cooling-curves, the cooling of the same ingot has in many cases been repeated three and even four times in order to eliminate the possibility of mistaking small irregularities due to experimental error for minor heat evolutions

Eleven typical examples of these cooling-curves are reproduced in figs. 1 and 2. The numbers attached to each curve refer to the alloys as numbered in Table I.; these

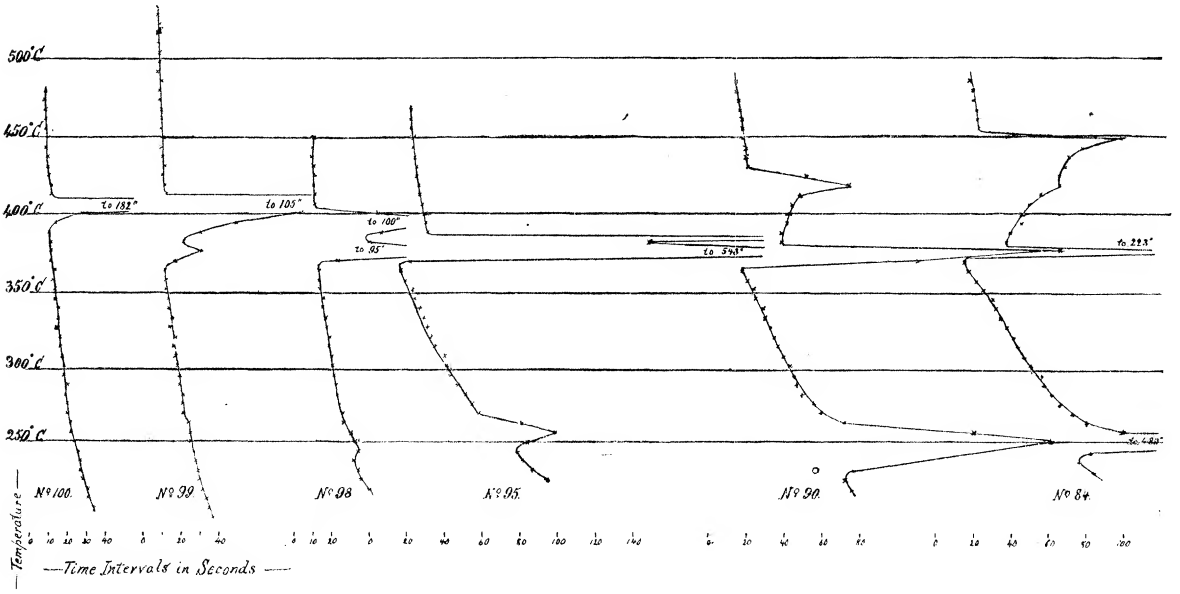


Fig. 1.

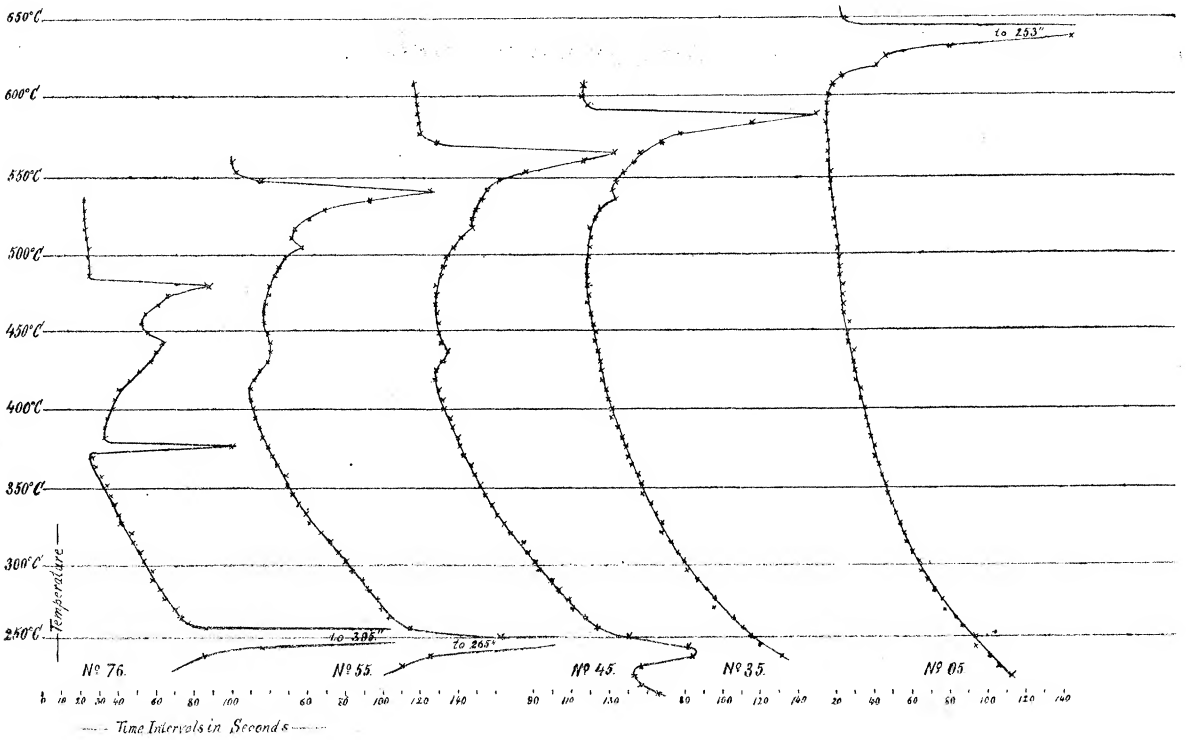


Fig. 2.

numbers approximately represent the percentage of zinc contained in the alloys. The actual observations on which these curves are based are given in an appendix.

Curve No. 100 is the cooling-curve of pure zinc. This merely shows the arrest due to the freezing of the pure metal; no evolutions of heat can be observed at lower temperatures down to 200° C.

No. 99 is the cooling-curve of an alloy containing 98·8 per cent. of zinc; here a small arrest is visible at 376° C., but nothing further. In No. 98 (97·9 per cent. zinc) three arrest points are to be observed: the highest is obviously the temperature of initial freezing, the second is related to the lower of the two points in the previous curve and occurs at the same temperature, while the third, at about 240° C., is a faint indication of a heat evolution which becomes more marked in the following curves. In the next, No. 95 (95·76 per cent. zinc), we have two large points very nearly merged together, one occurring at 383° C. and the other at 380° C. As the time observations taken for these curves were made at intervals of 5° C., it would not have been possible to separate these two points had the observer's attention been confined to taking the data for the curve; in practice, however, the exact temperature at which the actual arrest of cooling occurs is carefully noted, and as an interval of 3° C. is represented by a distance of 24 mm. on the scale of the instrument, the two arrests in the present alloy were readily distinguished. Curve No. 95 also shows a decidedly more marked peak at 257° C.; it will appear later that this is connected with the points at 240° C. on No. 98, the lower temperature in the former case being an example of the manner in which the temperature of a reaction is apt to be lowered when that reaction is rendered faint by the extreme dilution of the constituent in which it occurs.

Curve No. 90 (88·75 per cent. zinc) again shows three distinct peaks: the temperature of the initial freezing has now risen to 426° C., the second point still occurs at the constant temperature which lies between 377° C. and 381° C., while the third point, now very large, is again seen at 257° C.

Passing on to No. 84 (83·5 per cent. zinc) we find a curve with four points; the temperature of initial freezing has risen further to 450° C., and we again have arrests at 381° C. and 257° C. In addition to these, however, there is now a very small point occurring at a temperature of about 425° C.; this again is the first sign of a heat evolution which will be met with in a more vigorous form in succeeding alloys.

In No. 76 (75·29 per cent. zinc) we again have four points. The faint reaction noticed in No. 84, at 425° C., has now developed into a marked heat evolution at 443° C., the temperature of the faint reaction in No. 84 being depressed by dilution. We still have a small point in No. 76, at 380° C., and the peak at 257° C. is still well marked.

In No. 55 (55·7 per cent. zinc) the character of the cooling-curves has changed considerably; the heat evolutions at 443° C. and 257° C. can still be traced, but the peaks found in previous curves at 380° C. are unrepresented here; on the other hand, a very small, but quite definite, peak is found at a temperature between that of initial freezing and that of the reaction at 443° C., and appears to be the indication

of a third group of reactions. It will be seen that a series of small heat evolutions can be traced throughout the succeeding alloys up to and including pure aluminium, forming a generically connected series with the point shown in this curve, but presenting the curious feature that they occur at successively higher temperatures as the concentration approaches pure aluminium.

Curve No. 45 (46·4 per cent. zinc) shows the same four points which have just been described in Curve 55, but the peaks at 443° C. and 257° C. are now much smaller. In Curve No. 35 (33·2 per cent. zinc) only the two upper points persist, all the lower points having disappeared; the same remarks apply to Curve No. 05.

In further reference to the points occurring in Curves 55 to 05 it should be pointed out that the apparently feeble character of this heat evolution arises in part from the fact that it occurs so soon after the commencement of freezing of the alloys; that portion of the cooling-curve upon which this peak is shown slopes backward very steeply, and a very considerable evolution of heat is therefore required to arrest and even to reverse this steep slope. This circumstance somewhat militates against accuracy in the determination of these peaks, the actual peaks shown on the curves being in some cases not very much larger than experimental perturbations which now and then occur. In order, however, to show definite evidence of the existence and constant occurrence of these heat evolutions, three cooling-curves of the same ingot are reproduced in fig. 3; a comparison of these three curves will clearly demonstrate

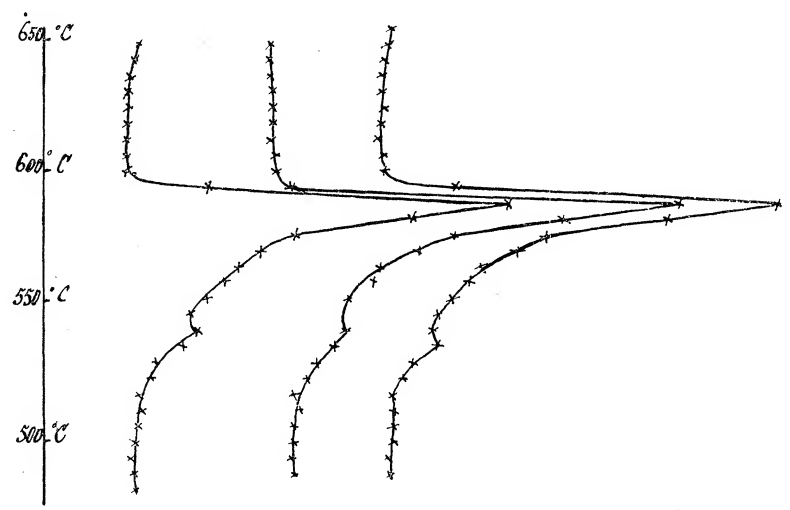


Fig. 3.

the constant occurrence of this heat evolution in spite of the apparent smallness of the peak on each individual curve.

The group of cooling-curves, as shown in figs. 1 and 2, cannot readily be translated into an equilibrium diagram, even with the aid of the additional intermediate curves which were obtained by the authors, and a larger amount of experimental evidence

was required in order to render intelligible the nature of the various heat evolutions and their mutual relations; it will, however, be more convenient to describe this further experimental work by first giving the equilibrium diagram finally arrived at. It will then be possible to discuss each group of alloys and the reactions which they undergo, and to give in detail the evidence upon which the position and interpretation of each line of the diagram is based.

The equilibrium diagram of the aluminium-zinc alloys is shown in fig. 4, where the concentration of aluminium is plotted horizontally and temperature is plotted

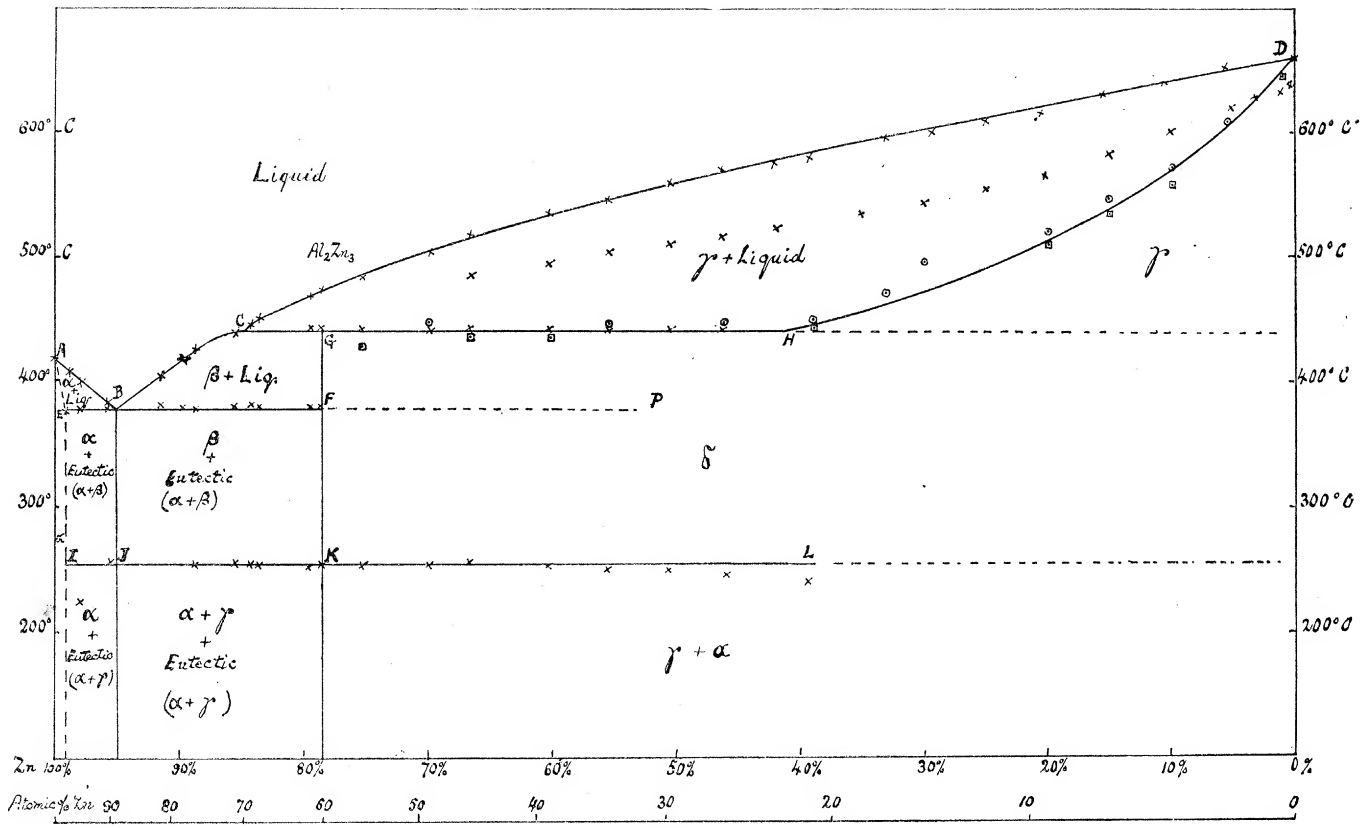


Fig. 4.

vertically in the usual manner. The observed temperatures of arrests or retardations on the cooling-curves are shown as crosses, while the results of quenching experiments are indicated by dots surrounded by small circles or squares. The points plotted include all those observed.

The liquidus, or curve of initial freezing, is represented by the line ABCD; this differs only very slightly from the corresponding curve in the diagram of SHEPHERD,* but the diagram of SHEPHERD did not show the small break in the liquidus at the point C. The evidence for the existence of this break in the liquidus lies in the first place in the accuracy with which the observed points on the liquidus have been

* SHEPHERD, "Aluminium-Zinc Alloys," 'Journal of the Physical Society,' 1905, 9, p. 504.

determined; this is such that a continuous curve from B to D would lie further from the observed points than the limits of experimental error would allow, particularly as the points on the liquidus near the point C have been repeatedly determined with special care. The existence of a break at C is further confirmed on theoretical grounds by the evidence to be described presently, proving that the phases which commence to crystallize along the branches BC and CD are two distinct bodies.

The solidus curve of the diagram consists of the lines AE, EB, BF, FG, GH, HD.

The evidence for this statement is to a large extent microscopical; the method of prolonged annealing followed by quenching has been adopted throughout and details of the evidence obtained in this way, particularly with regard to the lines GH and HD, will be given below.

The line EBF, both as regards temperature and as regards the position of the point B, agrees closely with the eutectic line shown in SHEPHERD'S diagram, but an important difference is found with regard to the end of this line on the aluminium side. On referring to the cooling-curves in figs. 1 and 2, it will be found that the arrests along the line EBF are still marked in Nos. 78 and 76, yet the eutectic line in the diagram is drawn only to the point F, corresponding to a concentration of 78·3 per cent. of aluminium.

The reason for this discrepancy lies in the fact that although alloys cooled with moderate rapidity exhibit a eutectic heat evolution to a considerable distance to the right of the point F, yet both microscopically and pyrometrically this eutectic can be made to disappear entirely by exposing the alloys to a temperature of about 430° C. for a considerable period of time.

In order to establish this point, ingots of a series of alloys lying on either side of the point F were maintained for about 100 hours at a temperature near 430° C., and cooling-curves of these ingots were subsequently taken at a rate similar to that described for the series of curves illustrated in figs. 1 and 2, the observations being taken from a temperature of 430° C. to about 200° C. The curves of alloys, Nos. 80, 78, and 75, are shown in fig. 5, the curves marked *a*, *b*, and *c* being those taken by ordinary slow cooling from fusion, while those marked *d*, *e*, and *f* are those taken after the heat treatment just described. In No. 80 the eutectic heat evolution has not been entirely removed by the treatment, but in Nos. 78 and 75 the well-marked peaks of the ordinary curves have entirely disappeared after the treatment. This indicates that the existence of stable eutectic is limited by a concentration lying between 78 and 80 per cent. of aluminium, and probably lying quite close to 78 per cent.

In order further to ascertain the concentration at which the eutectic disappears the method of measuring the heat evolutions in successive alloys was adopted. Although every precaution was taken to render these measurements as accurate as possible, it must be recognised that the method itself is not capable of any high degree of accuracy, the reason being that although the cooling-curves generally give a definite

indication of the commencement of an evolution of heat, no sharp indication of the *end* of such an evolution can be obtained.* In the present experiments the ingots used each weighed 150 gr., and all of them had been annealed together at a temperature of 430° C. for about 100 hours, experiment having shown that this period was sufficient to secure complete equilibrium.

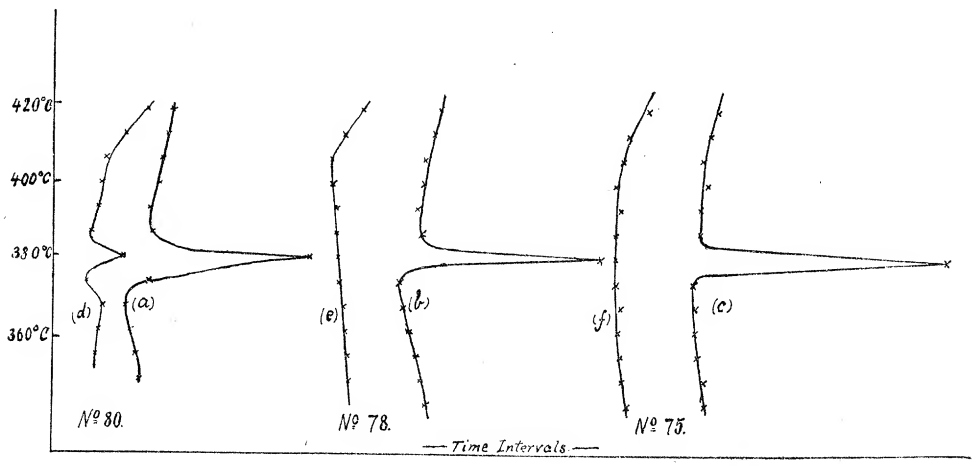


Fig. 5.

These ingots were cooled in an electrically heated furnace placed inside a water-jacket, and the initial temperature as well as the rate of cooling were kept as nearly uniform as possible throughout the series. The resulting curves were plotted on a large scale and the peaks of the inverse rate curves were measured with a planimeter, or, in some cases, the areas were determined by plotting on thin card, cutting out the peaks and weighing the pieces of card on a sensitive balance. The observed areas of the peaks depend upon the choice of a point on the cooling-curve to represent the end of the heat evolution, and it has already been pointed out that this choice cannot be made with any degree of certainty. In the present series of curves these points were inserted by estimation and the endeavour was made to place them on corresponding parts of the curves for all the alloys. The areas of the peaks thus measured represent approximately the quantities of heat evolved by each of the alloys and, within the limits of accuracy of the method, these may be taken to be proportional in the present case to the quantity of eutectic undergoing solidification in each alloy. These quantities as ordinates are plotted on abscissæ representing the concentration of the alloys in the upper curve of fig. 6.

It will be seen that the points thus obtained lie with considerable accuracy upon the straight line which cuts the zero line at a concentration of 78·8 per cent. of zinc, this concentration representing the limit of the eutectiferous alloys as determined by this method of extrapolation. It will be shown later that the termination of the

* See "Observations on Recalescence Curves," by W. ROSENHAIN, 'Proc. Phys. Soc.,' 1908.

eutectic line at this concentration is really due to the formation of a definite aluminium-zinc compound whose existence is confirmed by other evidence.

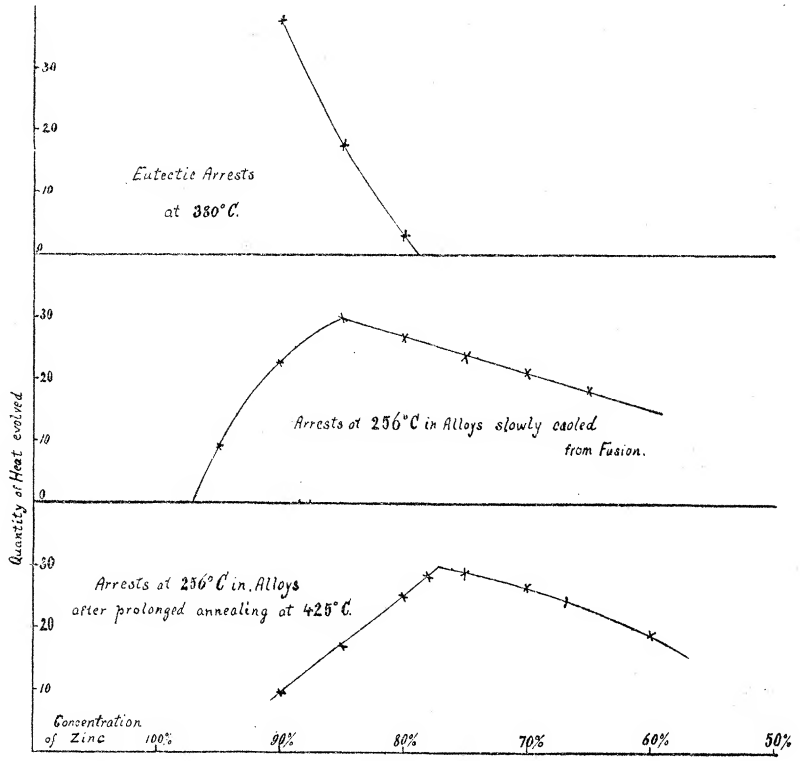


Fig. 6.

We have now to consider the nature of the heat evolutions along the lines CH and IL of fig. 4.

The fact which has already been stated that in slowly cooled alloys eutectic is found to the right of the point F, while this eutectic disappears when full equilibrium has been obtained, points to the conclusion that there is in these alloys a gradual reaction at some temperature above that of the eutectic line, and that this reaction, when allowed to complete itself, results in the total absorption of the liquid phase which would otherwise have solidified along the dotted line FP. The existence of a series of heat evolutions along the horizontal line CH at once suggests that such a reaction is represented by these heat evolutions, and this view is confirmed when it is remembered that in curves of more rapid cooling these heat evolutions are much less marked, an observation which indicates the occurrence of a *gradual* reaction. We have, further, the discontinuity in the liquidus curve at the point C, which also suggests that we are here dealing with a compound which is produced by a reaction of the solid which had begun to crystallize along the branch of the liquidus CD, with the liquid phase which is present when the temperature of the line CH is reached. It is well known that such a reaction taking place between a solid and its mother liquor results in the formation of sheaths of the new compound, and that these

sheaths, by separating the two reacting bodies, considerably retard the further progress of the reaction, which can then only take place by diffusion through the sheath. An indication of the composition of this compound has already been obtained by the determination of the end of the eutectic line, which has been found to lie at a concentration of about 78 per cent. of zinc, and this corresponds approximately with the composition of the compound $Al_2Zn_3$ which contains 78·35 per cent. of zinc. It was not found possible to apply the method of approximate quantitative estimation of the heat evolutions along the line CH for the purpose of determining the concentration at which this heat evolution attains its maximum value. In the first place, the peaks representing these heat evolutions on the cooling-curves lie so near the large peaks representing the initial freezing of the alloys that the precise shapes of these smaller peaks cannot be ascertained even with that degree of approximation which was reached in the other case; further, this reaction is not complete when the alloys are cooled even at the slowest rate practicable for cooling-curve observations, and no reliance can be placed on the quantities of heat evolved by a series of heat evolutions which might proceed to a greater or lesser degree of completion in the various alloys of the series.

In the absence of the kind of evidence just referred to, it is fortunate that it is possible to show an intimate connection between the heat evolutions which take place along the line CH and those which occur at a temperature of 256° C. along the line IL. This connection was established in the first place by means of cooling-curves of a number of the alloys taken first by allowing them to cool at the standard slow rate from fusion, and again after prolonged heating at 430° C. It was found that the size of the peak at 250° C. increased very much after the alloy had been exposed to prolonged heat at a temperature just below that of the line CH. This is illustrated in fig. 7, where cooling-curves of alloys Nos. 70 and 75 are given. The peaks on the cooling-curves of these alloys when cooled slowly from fusion are shown on the curves marked (*a*) and (*c*), while the corresponding peaks on the same alloys after prolonged annealing at 430° C. are shown on the curves marked (*b*) and (*d*). The curves themselves show that the rate of cooling was practically identical in all four cases. This observation indicates that the magnitude of the lower heat evolution is directly dependent upon the extent to which the reaction along the line CH has been allowed to take place, and the inference is justified that the heat evolutions along the line IL are due to a reaction occurring in the compound which is formed along the line CH. This inference will be more completely established by the microscopic evidence to be described below.

The connection between the heat evolutions along the line IL and those along the line CH having been established, an attempt was made to utilize the measurement of the quantities of heat evolved by the reactions at 256° C. for the purpose of locating the maximum of that reaction, a maximum which would coincide with the maximum of the heat evolutions along the line CH. An attempt to do this was first made by

taking a series of cooling-curves of alloys cooled slowly from fusion under careful standard conditions, the heat evolutions being measured in the manner described in connection with the eutectic line EF. These determinations give the points represented in the second curve of fig. 6, and it will be seen that these points indicate the

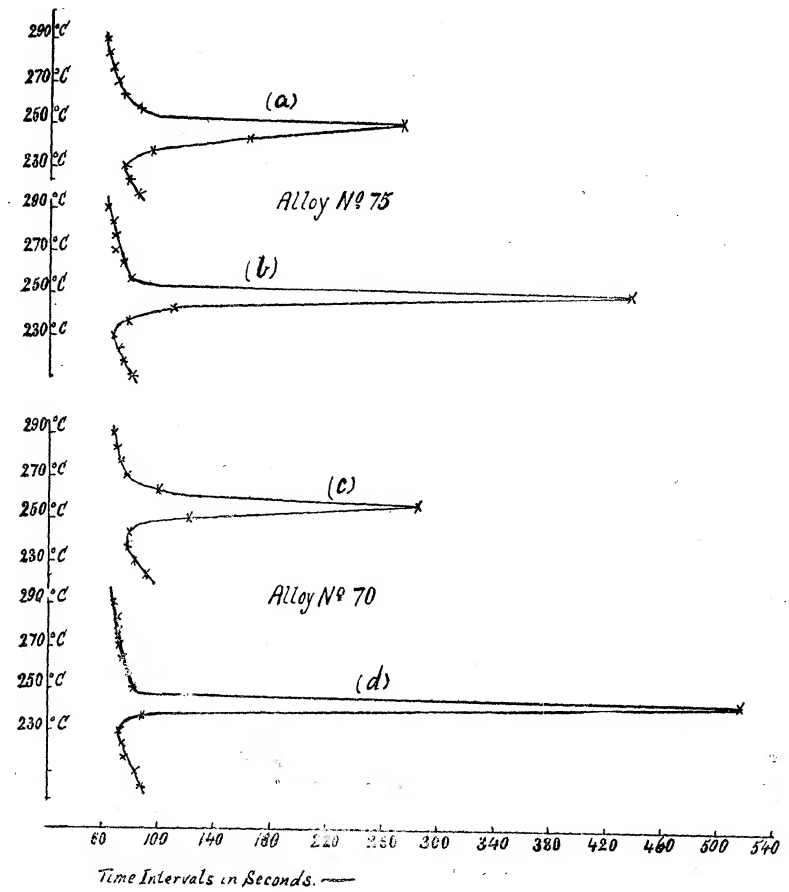


Fig. 7.

existence of a well-defined maximum lying exactly under the point C. This unexpected result can, however, be explained in a simple manner when it is remembered that the compound whose reaction is being measured crystallizes freely from the liquid along the line BC of the liquidus, while to the right of the point C this compound is the result of a slow reaction between a solid and a liquid. In these circumstances it is not surprising to find that in a series of alloys cooled at a standard rate the quantity of this compound would increase steadily as we pass from the concentration of the point B to that of point C, but that immediately on passing beyond C the quantity of the compound would decrease. The maximum obtained from such a series is therefore a misleading one, and does not represent the composition of any phase. The authors believe that this is an observation of some importance in the application of the methods of investigation styled "Thermal Analysis" by

TAMMAN, since it indicates that the results of such heat measurements, even when allowance is made for their unavoidable inaccuracies, must be considered with great caution before they can be accepted.

In the present case the difficulty was overcome by measuring the heat evolutions on the series of cooling-curves already described in connection with the measurements of the peaks along the eutectic line EF; these curves were taken from ingots so treated that the reaction along the line CH had been allowed to reach completion, and on these curves the maximum should truly represent the quantity of the compound present in the alloy. The data from these cooling-curves relating to the reaction along the line IL, plotted in the usual manner, are shown in the third curve in fig. 6; this curve shows a maximum near a concentration of 77·2 per cent. zinc. It will be seen that this agrees nearly, but not quite accurately, with the end of the eutectic line, as indicated on the upper curve of this figure, which falls at 78·8 per cent. zinc. The slope of one of the lines in the lowest curve of fig. 6, however, is somewhat flat, so that a small alteration of one or two of the observed points would displace the maximum to an extent quite comparable with this discrepancy. The authors, therefore, feel justified in saying that both the end of the eutectic line and the maximum of the heat evolutions along the line IL are consistent with the existence of a definite compound $Al_2Zn_3$.

The determination of the position of the point H and of the curved portion of the solidus from H to D, having been based entirely on microscopical evidence, will be described in connection with that portion of the work, and we pass on to consider the line of points shown on the diagram in fig. 4, mostly lying within the area CDHG. It will be seen that these points lie on a perfectly smooth curve, starting from the temperature 638° C., at which a minute heat evolution is observed in most varieties of aluminium, including the comparatively pure variety used in preparing the present series of alloys.*

Samples of aluminium have, however, been obtained which do not show this heat evolution, and this fact would suggest that the thermal change in question does not occur in the purest varieties of aluminium, but that its occurrence is determined, and its intensity accentuated, by the presence of certain other elements. One of the authors, in a recent research on the alloys of aluminium and manganese, found a series of small heat evolutions starting from this temperature in nearly pure aluminium, and continuing at the same temperature, but with increased intensity, with successive additions of manganese until the concentration of the point $Mn_3Al$ is reached.† In the present series of alloys the addition of zinc also appears to intensify the heat

* This point has frequently been observed in aluminium, and special attention was drawn to it by E. F. LAW. ("The Failure of the Light Engineering Alloys," 'Faraday Society,' 1910.)

† W. ROSENHAIN and F. C. A. H. LANTSBERRY, "Ninth Report to the Alloys Research Committee of the Institution of Mechanical Engineers—On the Properties of some Alloys of Copper, Aluminium, and Manganese," 1910.

evolution slightly, but its principal effect is the gradual depression of the temperature at which the change takes place.

It was thought at first that a curve joining these points near the aluminium end might represent the solidus of the alloys, while the points near the other end of the series were suspected of forming another horizontal line running into the liquidus and indicating the presence of another aluminium-zinc compound. These heat evolutions, however, although very minute are very definite, and the temperatures at which they occur are so well defined that the experimental evidence is sufficient to negative the supposed existence of a horizontal line in this case. The certainty with which these minute peaks recur on repeated cooling-curves of the same alloy has already been illustrated in fig. 3, where three successive cooling-curves of the alloy No. 35 are plotted side by side. The supposition that the upper part of the curve might represent the solidus was also negatived by the indications of quenching experiments which, by demonstrating the absence of an upward step in the solidus between H and D, further negative the supposed existence of a compound whose formation might be represented by these arrests.

The explanation which at first sight suggested itself for this line of arrest-points is that they are due to an allotropic change in aluminium, or in the phase rich in aluminium, and that this change occurs at lower temperatures with increasing concentration of zinc. If the line of the points in question lay entirely below the solidus, this explanation might be regarded as feasible, but in the alloys from about 3 per cent. to 66 per cent. of zinc, these points occur very definitely *above* the solidus and a transformation or inversion of any kind in a solid phase which is surrounded by its mother liquor can only occur at a constant temperature since the composition of such a solid phase at a given temperature is the same for the whole series of alloys in which it occurs, and the same inversion must occur in all such bodies at the same temperature. Meta-stable conditions cannot be invoked to explain away this difficulty, since the meta-stable formation of "cores" in such alloys implies the presence of a solid containing less zinc than the average composition of the alloy, and since the line of points in question slopes upwards towards the aluminium end of the diagram these meta-stable cores would undergo transformation or inversion at a *higher* temperature than that which would occur under equilibrium conditions in the same alloys. These considerations, therefore, afford no explanation for the depression of these points with increasing concentration of zinc.

The only explanation which the authors feel justified in suggesting is that the occurrence of these points, or rather their continual depression with increasing zinc content, may be due to the action of a third component substance which enters into the alloys as an impurity. Such an impurity is found in the form of 0·20 per cent. of iron present in the aluminium employed, while a certain amount of silicon is also present in the alloys. The author's suspicion has fallen principally upon iron since a few isolated crystals of an iron-aluminium compound have been observed in most of

the alloys. Some experiments have been made by taking cooling-curves of a few ternary alloys of aluminium, zinc, and iron with a view to establishing the connection between the small heat evolutions under discussion and the presence of the compound referred to. It would seem, however, that the iron-aluminium diagram itself requires to be worked out afresh and that the relationships between these three metals are of a complex kind, so that a great deal of further experimental work will be necessary before the truth of the suggested explanation can be tested. In view of these circumstances the authors have not thought it desirable to delay the publication of the present research until this further and larger investigation could be completed. They therefore content themselves with indicating this series of heat evolutions on the diagram, but without drawing a line through them or offering more than the tentative explanation outlined above.

We now pass on to the consideration of the micro-structures of the alloys. As has already been indicated, much of the evidence for the lines of the diagram, and particularly for their interpretation, is based upon microscopic evidence, and the micro-structures will be described from this point of view.

For the purpose of microscopic examination small specimens were, as a rule, cut from the ingots used for cooling-curve determinations. In some cases complete vertical sections of the ingots were examined in order to avoid risks of error from segregation. The polishing of the specimens near both ends of the series proved very difficult. Most of the specimens were etched with a 10-per-cent. solution of caustic potash—in one or two cases weak nitric acid was used.

Commencing at the zinc end of the diagram we have first a very narrow area marked in fig. 4 as representing alloys consisting entirely of the meteral $\alpha$. This designation includes pure zinc and the solid solution of aluminium in zinc. The exact limits of the solubility of aluminium in solid zinc have not been finally determined, although an alloy containing 1 per cent. of aluminium has been found to show signs of the presence of eutectic after 24 hours of annealing at a temperature just below the freezing-point of the eutectic. This observation indicates that unless the rate of solution is extremely slow the limit of the $\alpha$ region lies within 1 per cent. of pure zinc. The line indicating the limit of this region is therefore shown as a dotted line only, and has, for convenience, been drawn further to the right than the evidence justifies.

The diagram next indicates a group of alloys consisting of the meteral $\alpha$ embedded in eutectic, the constituents of the eutectic being termed $\alpha$ and $\beta$ above the line IJ, and $\alpha$ and $\gamma$ below that line. The general structure and appearance of one of these alloys is shown in Plate 5, fig. 8, under a magnification of 150 diameters. This represents the alloy containing 98 per cent. of zinc slowly cooled, and shows $\alpha$ with small quantities of eutectic. If such a specimen is quenched from a temperature above IJ (256° C.) the appearance of the micro-structure under moderate magnification, such as that of fig. 8, is as shown in that figure, but under higher

magnifications there is a distinct difference between such a quenched alloy and one which has been slowly cooled. It is found that while the $\beta$, or dark-etching, constituent of the eutectic is homogeneous in the quenched alloy, in the slowly cooled specimens the $\beta$ meteral has undergone decomposition and exhibits a duplex structure which may take the form either of parallel lamellæ or of minute granules. Fig. 9 shows the structure of this decomposed eutectic under a magnification of 1000 diameters; the large dark areas represent the structure of the eutectic while the minute granulation in these areas indicates the decomposition of the $\beta$ constituent. The photomicrograph in fig. 9 is actually taken from an alloy containing 95 per cent. of zinc, but the same features are found in all the alloys in which the eutectic is present.

The typical structure of the eutectic alloy, seen under moderate magnification (200 and 150 diameters respectively), is shown in figs. 10 and 11. It will be seen that the eutectic exhibits in a very beautiful way the characteristic features of well-defined eutectic alloys, and it will further be noted that the relative areas of the dark and light constituents are not very widely different. When it is realized that this structure is found in an alloy containing only 5 per cent. of aluminium, this observation alone strongly suggests that the components of the eutectic are not in reality zinc and aluminium, but zinc and a compound of zinc and aluminium containing a considerable proportion of zinc. Eutectics lying near one end of a binary series are not unknown in other groups of alloys, but they do not exhibit a well-balanced laminated structure unless a compound comes into play.

The micro-structures found in alloys containing less than 95 per cent. of zinc, that is to say, lying just to the right of the eutectic concentration, further support the view that the $\beta$ meteral, which forms the dark-etching constituent of these alloys, is a definite compound. These micro-structures are illustrated under a magnification of 200 diameters in figs. 13 and 14. These two figures show the presence of strikingly characteristic dendritic crystals, which possess a strong tendency to assume six-rayed forms in which angles closely approximating to 60 degrees are of frequent and typical appearance.

This is a striking characteristic, particularly in view of the fact that in the great majority of metals the dendritic branches tend to form rectangular systems. The microscopic evidence thus strongly supports the pyrometric evidence for the existence of a definite compound, and grounds have been given above for the view that this compound is represented by the formula $Al_2Zn_3$.

The close relationship between the six-rayed crystals just described and the eutectic surrounding them is also illustrated in an interesting manner by fig. 14. It is there clearly evident how the crystallization of the eutectic has radiated from the various branches of the dendrite, resulting in the formation of an interesting pattern.

The photomicrographs, figs. 13 and 14, having been taken from slowly cooled specimens of the alloys, are not free from signs of the reaction represented in the

diagram by the line IJK. The material of the six-rayed dendrite, even under this moderate magnification, is seen to be far from homogeneous, and under higher magnifications it is found to have undergone the same kind of change as that which has already been described and illustrated for the $\beta$ constituent of the eutectic.

Fig. 16 ($\times 150$) shows the micro-structure of alloy No. 90, containing 89·85 per cent. of zinc, as it appears when the alloy is cooled from fusion in the furnace in about 45 minutes. The photograph shows a larger proportion of the $\beta$ meteral than that seen in fig. 14 embedded in eutectic, but the edges of the $\beta$ masses show rims of a changed material arising from the reaction indicated by the line IJK of the diagram. The existence of these rims proves that this reaction is rather slow, and the facility with which it can be inhibited by quenching further confirms this view.

In fig. 17 ($\times 150$) we see the micro-structure of alloy No. 86 (85·52 per cent. zinc) cooled rather more slowly than the specimen represented in fig. 16. This specimen (fig. 17) has, in fact, been cooled at the rate adopted for the observation of cooling-curves. The proportion of $\beta$ is larger than in fig. 16, but the change which resulted in the formation of "rims" in fig. 16 has here taken place to a much larger extent, so that the original $\beta$ body has almost entirely disappeared. Under the magnification of fig. 17 (150 diameters) the resulting structure of the "changed" $\beta$ is not very evident, but a portion of the same specimen is shown in fig. 18 (Plate 5) under a magnification of 500 diameters, and there the uniformly dark $\beta$ is seen to have become broken up into a laminated structure closely resembling the pearlite seen in steel. On account of this resemblance, the authors propose to describe this structure as "pearlitic"; it will, however, be seen that in this case the duplex structure arises from the decomposition of a compound and not, as in the case of pearlite, from the decomposition of a solid solution.

The nature of the reaction represented by the line IJK can now be understood—it is the decomposition of the definite compound $\beta$ into two phases which phase-rule considerations prove to be identical with those called $\alpha$ and $\gamma$ on the diagram, the former being solid zinc saturated with aluminium and probably containing less than 1 per cent. of that metal, the latter being aluminium saturated with free zinc, the exact proportion not being quite definitely determined, but probably lying in the vicinity of 40 per cent. The phase-rule considerations just referred to are that, in any field or area of a binary system, two phases only can exist in equilibrium. In the field BJKF we have the phases $\alpha$ and $\beta$ present. Now, if $\beta$ is decomposed, as the microscope proves that it is, into two phases, say X and Y, then in the field below JK we should have $\alpha+X+Y$ present, and it follows that either X or Y must be identical with $\alpha$. Similar considerations applied to the fields to the right of the line GFK show that the other phase must be identical with $\gamma$.

The alloys whose micro-structure is shown in figs. 13 to 18 all belong to the group whose liquidus is the line BC. We now have to consider the alloys to the right of the point C. In these the phase first separating from the liquid is $\gamma$ and not $\beta$. On

reaching the temperature of the line CGH the $\gamma$ crystals react with the liquid according to the equation

$$\gamma + \text{liquid} = \beta\,(Al_2Zn_3).$$

Up to the line GFK, which represents the composition of the compound $Al_2Zn_3$, this reaction, even if completed, leaves a residue of liquid which solidifies as eutectic. The amount of this eutectic, however, decreases until it vanishes at the composition of the compound.

The microscopic evidence supporting this statement is of considerable importance because it constitutes a strong confirmation of the existence of the definite compound $Al_2Zn_3$; it is, therefore, given in some detail. We have first in fig. 19 ($\times 150$) an alloy containing 80 per cent. of zinc and, therefore, lying just to the left of the line GFK; this has been maintained for five hours at a temperature just below the line CH and has then been slowly cooled. The photomicrograph shows the presence of small quantities of eutectic. In this respect this alloy is in contrast with one containing 78 per cent. of zinc, in which the eutectic disappears entirely under the same treatment, the resulting structure being perfectly homogeneous, like that shown in fig. 26.

The structure shown in fig. 19 represents an aggregate of $\beta$+eutectic, except that in consequence of slow cooling the reaction along JK has taken place and the dark-etched $\beta$ body is in reality duplex, consisting of $\alpha$ and $\gamma$.

The reaction $\gamma$+liquid = $\beta$ which takes place along the line CH, being a reaction between a solid and its mother liquor, results in the formation of sheaths of $\beta$ surrounding the $\gamma$ crystals. In the alloy of fig. 19 the prolonged heating at 430° C. has obliterated the sheaths, but if a similar alloy is cooled comparatively quickly the existence of these sheaths is very clearly seen. In fig. 20 ($\times 150$) we have an alloy of the same group which has been quickly cooled down to a temperature just above 256° C., and has then been quenched in order to prevent the decomposition of the $\beta$ sheaths. These are very clearly seen in the photograph as dark edges surrounding the relatively light bodies of primary $\gamma$. The same alloy slowly cooled from fusion to the ordinary temperature is shown in fig. 21 ($\times 150$); the cooling having been slower in this case the original sheaths of $\beta$ are hardly visible, almost the whole of the dark dendrites having been transformed into $\beta$ when the alloy passed the line CH. At 256° C., however, the rate of cooling was not slow enough to allow the decomposition of $\beta$ to be completed, and the structure therefore shows dendrites of $\beta$ merely decomposed at the edges. In fig. 22 ($\times 300$) we have the same alloy, this time after prolonged heating just below 430° C., and then cooled more slowly than in the previous example. Here both the formation and decomposition of $\beta$ have been completed, and a higher magnification would reveal the completely pearlitic structure of the dark areas of this photograph; in the photograph the duplex character of the dark constituent is evident in many places. In contrast to this we have fig. 23

(×300) which represents an alloy in which the formation of $\beta$ has been completed by prolonged heating just below 430° C., but the decomposition of $\beta$ has been prevented by quenching the specimen just above 256° C. The grey areas seen in this photograph are perfectly homogeneous and show no signs of pearlitic structure, even under the highest magnification. These five photomicrographs, showing the variation in the structure of an alloy lying just to the left of the line GFK, confirm the diagram of fig. 4 and its explanation as put forward by the authors.

We now pass to the alloys lying just to the right of the line GFK. Fig. 24 represents alloy No. 78 containing 78·48 per cent. of zinc magnified 150 diameters. The specimen in this case has been slowly cooled from fusion and is therefore in a meta-stable condition; dark cores of primary $\gamma$ are surrounded by sheaths of decomposed $\beta$, leaving a residue of eutectic. The decomposition of the $\beta$ body is not obvious in this photograph, but is very clearly seen in fig. 25 representing a portion of the same specimen as fig. 24 but magnified by 500 diameters. Here the laminated structure of the rims of decomposed $\beta$ is very evident. In fig. 26 (×150) we have the micro-structure of alloy No. 77, which in this respect is typical of all alloys containing less than 78 per cent. of zinc, after annealing for a considerable time at 430° C. followed by quenching from a temperature just above 256° C. The specimen exhibits a perfectly homogeneous structure merely diversified by a few holes and cracks. If this structure were met with only in the alloy of the composition of the compound $Al_2Zn_3$, the structure might be described as that of the pure $\beta$ meteral, but as a matter of fact this same homogeneous structure is exhibited by all the alloys containing less than 78 per cent. of zinc which have been treated in the same way. It follows from this observation that the $\beta$ body forms a solid solution with the $\gamma$ body, since to the right of the line GFK the reaction $\gamma$+liquid = $\beta$ must leave a residue of $\gamma$. For purposes of distinction the authors have termed this solid solution of $\beta$ and $\gamma$ the $\delta$ meteral. The $\beta$ which is dissolved in this $\delta$ body, at any rate so long as it is present in any considerable quantity, still undergoes decomposition at the temperature of the line JKL, and the phases present below this line are again $\gamma+\alpha$, but of course the amount of $\alpha$ decreases rapidly with decreasing concentration of zinc. It has not, however, been found possible to determine microscopically the concentration at which $\alpha$ ceases to appear in the alloys.

Fig. 27 shows, under a magnification of 600 diameters, the appearance of fully decomposed $\beta$ or $\delta$ rich in $\beta$. The photograph represents alloy No. 77 (77·3 per cent. of zinc) after prolonged heating, first at 430° C. and then just below 256° C. The beautifully laminated structure and its striking resemblance to the pearlitic structure of steel will be recognized at once. It is interesting to notice that this laminated structure is only produced when the alloy is cooled slowly through the decomposition temperature and is then held for some time just below that temperature. If the specimen be quenched from above and be then heated to a temperature just below 256° C. and held there for a considerable time, the resulting micro-structure, although

definitely duplex, is granular and patchy, recalling the structure of sorbitic and troostitic steels rather than the pearlitic structure shown in fig. 27. Although the rates of cooling and heating involved are decidedly slower in the present case, the behaviour of the $\beta$ meteral appears to present some interesting analogies to that of carbon steels.

To illustrate the behaviour of the group of alloys lying somewhat further to the right of the line GFK, the photomicrographs of figs. 28 to 31 represent the micro-structure of alloy No. 75 (74·5 per cent. of zinc). Fig. 28 ($\times 150$) represents the structure of a specimen of this alloy which has been cooled from fusion to 470° C., held at that temperature 30 minutes and then quenched. This temperature lies just above the line CH, and the micro-structure accordingly consists of crystals of $\gamma$ embedded in a finely-granulated matrix which represents that part of the alloy which was liquid at the moment of quenching. In fig. 29 ($\times 150$) we have the structure of a specimen of the same alloy which has been cooled from fusion to 430° C., held at that temperature for 30 minutes and then quenched. In this structure we see an approach to homogeneity; the black areas represent holes or cavities in the specimen, but there is no sign of the presence of liquid at the moment of quenching, nor is any eutectic present. This structure represents a stage of the reaction $\gamma + \text{liquid} = \delta$, where the reaction, although still incomplete, has progressed to a considerable extent. Fig. 30 ($\times 150$) represents the structure of a specimen of the same alloy which has been kept at 430° C. for about 2 hours, this treatment being followed by quenching from that temperature; here the reaction named above has been allowed to complete itself, while the decomposition which would otherwise have set in at 256° C. has been prevented by quenching; the resulting structure is therefore homogeneous and is typical of the alloys consisting of $\delta$. The same alloy, when slowly cooled after prolonged heating at 430° C., again shows the typical pearlitic structure resulting from the decomposition of $\delta$ or $\beta$. This is illustrated in fig. 31 under a magnification of 300 diameters.

The persistence with which meta-stable eutectic is found in the alloys of this group when slowly cooled is illustrated by fig. 32 ($\times 150$) which represents alloy No. 70 in this condition, which corresponds closely to that illustrated for alloy No. 78 in fig. 24; we have cores of primary $\gamma$ with rims of decomposed $\delta$ enclosing areas of eutectic. The same alloy, after heating for a considerable time at 430° C. followed by slow cooling, is illustrated in fig. 33 ($\times 170$), where the pearlitic structure can again be seen while there is total absence of eutectic.

The micro-structures of alloys lying to the right of the point H present few points of interest so far as the constitution of the alloys is concerned; they exhibit the characteristic features of alloys consisting of a single solid solution possessing a long range of solidification. The typical formation of cores in such alloys is illustrated in fig. 34 ($\times 150$), which represents the structure of a slowly-cooled specimen of alloy No. 40; if heated for any length of time to a temperature below that of the solidus,

this alloy and all those lying to the right of the point H become perfectly homogeneous.

It will be seen in the diagram that the lines GH and KL have been continued as dotted lines to the aluminium end of the diagram. This has been done because it may be supposed that, if final equilibrium is attained in the freezing process, the solid solution will react at the temperature of the line GH with the zinc which it contains to form the compound $Al_2Zn_3$, and this in turn will undergo decomposition when the temperature of the line KL is reached. This supposition, however, involves the assumption that the $\gamma$ solid solution contains the zinc as "free" zinc, while in the $\delta$ solid solution the zinc is present in the "combined" state, *i.e.*, in the form of molecules of the compound $Al_2Zn_3$. Just to the right of the line GFK of the diagram there can be no doubt that we have in the $\delta$ meteral a solid solution in which the compound $\beta$ is the solvent and free aluminium is the solute; this solid solution, however, is merely one end of a continuous series whose opposite extreme is represented by a solid solution in which aluminium is undoubtedly the solvent and the compound the dissolved body. The question arises whether the phenomena of dissociation or ionisation which are known to occur in dilute aqueous solutions also occur in these solid metallic solutions. Where the solution is a strong one, *i.e.*, in the present case for alloys containing more than 35 per cent. of zinc, there is ample evidence that the compound $\beta$ preserves its identity in the solid solution, but for lower concentrations there are two reasons why experimental evidence is not available.

In the first place, for all alloys lying to the right of the point H in the diagram, the reaction between the two constituents of the $\gamma$ solid solution must take place in entirely solid metal. Such reactions are not unknown, but in most cases they are very slow, and in the present instance the reaction in question is known to be slow even when one of the reacting phases is a liquid. It is, therefore, not surprising to find that even at the slowest rates of cooling which are possible for the observation of cooling-curves the reaction in these alloys takes place too slowly to be indicated by a heat evolution. The absence of arrest-points along the line GH beyond the point H is, therefore, no definite evidence that the reaction does not take place gradually if time be given at a favourable temperature. Further, microscopic evidence is difficult to obtain since microscopically the $\gamma$ and $\delta$ solid solutions are both homogeneous bodies. The only test would be that of tracing the effects of the decomposition at the temperature of the line KL by looking for the appearance of the $\alpha$ phase in the annealed and slowly-cooled alloys. An endeavour was made to do this, and the authors think it probable that the $\alpha$ phase can be traced up to a concentration of aluminium as high as 80 per cent., but it must be admitted that this method is not very reliable in this instance. The reason lies in the fact that even the homogeneous alloys of this series never present a perfectly clean polygonal structure—the surfaces of the crystals always show a certain amount of marking or pattern, while minute

crystals of impurities are often scattered about the specimens. This "dirty" appearance of the sections may be due partly to the great difficulty of polishing them perfectly, but it certainly makes it difficult if not quite impossible to state definitely at which concentration the appearance of a given phase ceases—it becomes difficult to decide whether certain markings are due to the causes mentioned above, or whether they indicate the separation of the $\alpha$ phase along the line KL. For these reasons the lines in question have been drawn as dotted lines only, and it is probable that for the higher concentrations of aluminium they merely represent theoretical possibilities.

As has already been indicated, the position of the solidus curve of these alloys has been determined by a series of quenching experiments. These were preferred to the employment of heating-curves because of the greater certainty of results from quenching, although a number of heating-curves were also observed. The quenching experiments in question consist, as is well known, in quenching a series of specimens from different temperatures, and subsequently examining the micro-structure of the quenched specimens in order to ascertain whether the presence of liquid at the moment of quenching is indicated or not. In the present series of alloys it was, however, essential that the specimens of alloy should be brought to a condition of equilibrium before being quenched, and for that reason a prolonged heating at a definite temperature was often required before the actual quenching operation itself could be carried out.

The quenching apparatus devised by one of the authors* was employed for this purpose throughout the research. The special advantages of this apparatus made themselves felt in a very marked degree in carrying out this work. The specimens are heated *in vacuo*, and this made it possible to employ very small specimens without fear of oxidation; these small specimens, generally measuring about 6 mm. cube, remained perfectly bright and were cooled with very great rapidity. The temperatures of the specimens, up to the moment of quenching, was measured by means of a thermo-couple placed in a small hole drilled to the centre of the specimen of metal, and since in this apparatus the specimen is quenched by a powerful stream of cold water which strikes the specimen in the furnace itself, and carries it out of the furnace with the water, the quenching-temperatures were known as accurately as those of the arrest-points on the cooling-curves.

The first series of quenching experiments were undertaken in order to prove that the line GH really constitutes part of the solidus curve; this fact is important not only for fixing the position of the solidus curve itself, but also as supporting the evidence for the existence of a definite compound at the concentration where the step-up in the solidus is found. The result of one of these quenching experiments has already been described and illustrated in connection with alloy No. 75 (74·5 per

* W. ROSENHAIN, "The Metallurgical Laboratories at the National Physical Laboratory," 'Journ. Iron and Steel Inst.,' 1908, I.

cent. of zinc) in figs. 28 and 29. The former figure shows the structure of this alloy quenched from a temperature above the line GH, and the presence of liquid at the moment of quenching is quite evident from the presence of a finely-granulated matrix in the section of the quenched specimen; on the other hand, in fig. 29, the structure is that of the same alloy quenched from a temperature just below the line GH, and here, although perfect homogeneity has not been attained, the absence of liquid is quite evident, although some cracks and cavities are found, but these are present in all quenched specimens of this somewhat brittle alloy. The results of further quenching experiments are indicated on the diagram by dots surrounded by small circles in those cases where liquid was found and by squares in those cases where the alloy proved to have been completely solid. A much larger number of quenching experiments were made than those shown on the diagram, but only those have been plotted which lie close to the limiting temperature, since the others are of no direct importance in determining the solidus, and merely served as guides for the choice of fresh quenching temperatures.

For the determination of the solidus curve from H to D over twenty quenching experiments were made, but only fourteen are plotted. The solidus curve has been drawn in such a manner as to pass between the nearest circles and squares (indicating liquid and solid respectively), some account being taken of the *amount* of liquid which was indicated by the observations on the various specimens.

In order to illustrate the appearance of "liquid" in the quenched specimens, photomicrographs representing the results of two quenching experiments are shown in figs. 35 and 36. Fig. 35 (×150) refers to alloy No. 50 (49·8 per cent. of zinc) quenched from a temperature of 467° C. The presence of liquid is indicated in this case by the broadening of the crystal boundaries and the presence of minute fusion spots in the crystals themselves. Fig. 36 (×150) shows a similar alloy quenched at a temperature just above the solidus. Here the indications of liquid are confined to small traces in the crystal boundaries, and there are no fusion spots.

## *General Conclusions.*

The general conclusions arrived at as a result of the pyrometric and microscopic investigations of the aluminium-zinc alloys, which have been described above, may now be summarized. They are represented graphically in the equilibrium diagram of fig. 4.

The addition of aluminium to zinc first depresses the freezing-point until a eutectic minimum is reached at a concentration of 95 per cent. of zinc and a temperature of 380° C. Further addition of aluminium raises the freezing-point until a concentration of 85 per cent. of zinc is reached where there is a small but distinct break in the freezing-point curve. From this point the freezing-point curve rises smoothly until

the freezing-point of pure aluminium is reached. The phases which commence to crystallize along the four branches of the liquidus curve just described are—

(1) The $\alpha$ phase, which is zinc, or zinc carrying in solid solution less than 1 per cent. of aluminium.

(2) The $\beta$ phase, which has been shown to be a definite compound of aluminium and zinc, probably of the formula $Al_2Zn_3$. This compound is characterized by a well-marked tendency to crystallize in six-rayed dendrites; it has only a limited range of stable existence, being decomposed on heating above 443° C. into $\gamma$ and liquid and on cooling below 256° C., breaking up into the two phases $\alpha$ and $\gamma$. The product of the decomposition of this compound, or of its solid solutions with the $\gamma$ phase, are found to assume a typical laminated structure closely resembling that of the "pearlite" of carbon steels. The $\beta$ compound is not capable of forming solid solutions with an excess of zinc, but with aluminium it forms a continuous series of solid solutions extending up to pure aluminium itself.

(3) The $\gamma$ phase, which is a solid solution of aluminium containing up to approximately 40 per cent. of zinc. Between concentrations of from 40 to 85 per cent. of zinc this solid solution reacts with zinc which may be present in either the liquid or solid form, to produce the compound $Al_2Zn_3$; from 78·3 to 85 per cent. of zinc the product of this reaction is the free $\beta$ compound, with a residue of liquid, but between 40 and 78·3 per cent. of zinc the resulting compound dissolves in the residual solid $\gamma$ phase, forming a series of solid solutions which have been termed the $\delta$ phase. Between the concentrations named, this solid solution undergoes decomposition on cooling to the temperature of 256° C., separating into the $\alpha$ and $\gamma$ phases. It is probable, although it has not been definitely proved, that both these reactions are continued in the alloys lying between the concentrations of 40 per cent. of zinc and pure aluminium.

The researches described in the present paper have been carried out in the Department of Metallurgy and Metallurgical Chemistry at the National Physical Laboratory. The authors are indebted to members of the chemical staff, particularly Messrs. G. Barr and L. L. Bircumshaw for carrying out the numerous analyses required in the research. As has already been indicated, they constitute a portion of a larger scheme of investigation of the alloys of aluminium which is being carried out at the Laboratory under the auspices of the Alloys Research Committee of the Institution of Mechanical Engineers. The authors desire to express their appreciation of the interest taken in this research by Dr. R. T. Glazebrook, C.B., F.R.S., Director of the Laboratory.

# APPENDIX.

## Table of Cooling-Curve Observations.

| Alloy No. . . . | 100 | 99 | 98 | 95 | 90 | 84 | 76 | 55 | 45 | 35 | 05 | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Temperature in micro-volts. | Time interval in seconds. | | | | | | | | | | | |
| 10800 | — | — | — | — | — | — | — | — | — | — | — | |
| | — | — | — | — | — | — | — | 24 | — | — | — | |
| 10600 | — | — | — | — | — | — | — | 22 | — | — | — | |
| | — | — | — | — | — | — | — | 23 | — | — | — | |
| 10400 | — | — | — | — | — | — | — | 24 | — | — | — | |
| | — | — | — | — | — | — | — | 23 | — | 39 | — | |
| 10200 | — | — | — | — | — | — | — | 23 | — | 33 | — | |
| | — | — | — | — | — | — | — | 23 | — | 30 | — | |
| 10000 | — | — | — | — | — | — | — | 23 | — | 29 | — | |
| | — | — | — | — | — | — | — | 24 | — | 29 | 24·5 | 9988 = 657° C. |
| 9800 | — | — | — | — | — | — | — | 24 | — | 27 | 253 | Freezing-point of *aluminium*. |
| | — | — | — | — | — | — | — | 24 | — | 26 | 145 | |
| 9600 | — | — | — | — | — | — | — | 25 | — | 26 | 81 | |
| | — | — | — | — | — | — | — | 25 | 26 | 27 | 47 | |
| 9400 | — | — | — | — | — | — | — | 25 | 27 | 26 | 42 | |
| | — | — | — | — | — | — | — | 26 | 26 | 25·5 | 23·5 | |
| 9200 | — | — | — | — | — | — | — | 27 | 27 | 26·5 | 18·5 | |
| | — | — | — | — | — | — | — | 26 | 28 | 26 | 16·5 | |
| 9000 | — | — | — | — | — | — | — | 27 | 28 | 49 | 15·5 | |
| | — | — | — | — | — | — | — | 27 | 28 | 150 | 15·5 | |
| 8800 | — | — | — | — | — | — | — | 29 | 29 | 116 | 14·5 | |
| | — | — | — | — | — | — | — | 29 | 30 | 78 | 16·5 | |
| 8600 | — | — | — | — | — | — | — | 30 | 39 | 69 | 17 | |
| | — | — | — | — | — | — | — | 29 | 133 | 57 | 15·5 | |
| 8400 | — | — | — | — | — | — | — | 30 | 117 | 54 | 15·5 | |
| | — | — | — | — | — | — | — | 31 | 86 | 48 | 17·5 | |
| 8200 | — | — | — | — | — | — | — | 45 | 72 | 44 | 17·5 | |
| | — | — | — | — | — | — | — | 135 | 66 | 42 | 17 | |
| 8000 | — | — | — | — | — | — | 22 | 103 | 63 | 44 | 19 | |
| | — | 7 | — | 34 | — | 25 | 22 | 79 | 60 | 36 | 20 | |
| 7800 | — | 8 | — | 33 | — | 26 | 22 | 71 | 58 | 33 | 19 | |
| | — | 7 | — | 30 | 13 | 25 | 22 | 63 | 58 | 29·5 | 19·5 | |
| 7600 | — | 7 | — | 31 | 13 | 27 | 23 | 62 | 52 | 30·5 | 21 | |
| | — | 8 | — | 31 | 13 | 27 | 24·5 | 67 | 48 | 30 | 21 | |
| 7400 | — | 8 | — | 31 | 14 | 28 | 23·5 | 58 | 44 | 30 | 22 | |
| | — | 7 | — | 30 | 15 | 29 | 24·5 | 55 | 42 | 28 | 22·5 | |
| 7200 | 8 | 9 | — | 32 | 15 | 29 | 24·5 | 53 | 41 | 29 | 22·5 | |
| | 7 | 8 | — | 31 | 15 | 30 | 88 | 50 | 39 | 29 | 24·5 | |

| | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 7000 | 8 | 8 | — | 31 | 16 | 30 | 66 | 50 | 39 | 30 | 24·5 | |
| | 8 | 9 | — | 32 | 17 | 32 | 61 | 48 | 38 | 28 | 24 | |
| 6800 | 8 | 9 | — | 32 | 18 | 32 | 54 | 47 | 39 | 31 | 25·5 | |
| | 9 | 9 | — | 32 | 18 | 33 | 52 | 47 | 40 | 32 | 28·5 | |
| 6600 | 8 | 9 | 10 | 33 | 18 | 109 | 55·5 | 49 | 40 | 33 | 26·5 | |
| | 9 | 9 | 9 | 33 | 20 | 88 | 63·5 | 50 | 41 | 32 | 27·5 | |
| 6400 | 9 | 10 | 9 | 34 | 20 | 81 | 60 | 50 | 45 | 34·5 | 30 | |
| | 10 | 11 | 10 | 35 | 21 | 79 | 57 | 49 | 42 | 35·5 | 30 | |
| 6200 | 11 | 10 | 11 | 35 | 52 | 76 | 51 | 45 | 39 | 36 | 31 | |
| | 11 | 11 | 10 | 36 | 75 | 76 | 46 | 42 | 38 | 36 | 31 | 6076 = 419° C. |
| 6000 | 182 | 12 | 11 | 37 | 49 | 66 | 40 | 40 | 40 | 39 | 34 | Freezing-point of *zinc.* |
| | 27 | 105 | 11 | 38 | 44 | 60 | 38 | 40 | 42 | 40 | 33·5 | |
| 5800 | 13 | 83 | 44 | 40 | 43 | 56 | 37 | 41 | 43 | 42 | 36 | |
| | 10 | 49 | 100 | 40 | 42 | 56 | 34 | 42 | 45 | 41 | 36 | |
| 5600 | 11 | 30 | 46 | 41 | 39 | 50 | 33 | 44 | 47 | 45 | 37·5 | |
| | 11 | 21 | 40 | 158 | 39 | 49 | 33 | 46 | 50 | 47 | 38·5 | |
| 5400 | 11 | 31 | 95 | 543 | 186 | 223 | 100 | 49 | 51 | 49 | 41 | |
| | 13 | 17 | 23 | 32 | — | 26 | 26 | 51 | 53 | 50 | 40·5 | |
| 5200 | 12 | 11 | 13 | 26 | 111 | 28 | 28 | 54 | 57 | 52 | 42·5 | |
| | 13 | 12 | 13 | 29 | 18 | 32 | 31 | 56 | 59 | 56 | 45 | |
| 5000 | 13 | 12 | 15 | 33 | 21 | 36 | 34 | 59 | 62 | 57 | 47 | |
| | 15 | 13 | 15 | 34 | 24 | 41 | 36 | 62 | 64 | 57 | 47 | |
| 4800 | 15 | 13 | 15 | 37 | 25 | 42 | 38 | 65 | 68 | 62 | 49 | |
| | 14 | 15 | 16 | 39 | 29 | 45 | 40 | 69 | 71 | 65 | 52 | 4616 = 328° C. |
| 4600 | 16 | 14 | 17 | 41 | 30 | 49 | 41 | 71 | 75 | 68 | 54 | Freezing-point of *lead.* |
| | 16 | 17 | 19 | 43 | 33 | 52 | 47 | 77 | 77 | 67 | 56 | |
| 4400 | 17 | 16 | 18 | 45 | 35 | 54 | 48 | 82 | 85 | 73 | 57 | |
| | 18 | 17 | 20 | 50 | 37 | 57 | 52 | 86 | 87 | 77 | 61 | |
| 4200 | 18 | 18 | 20 | 51 | 40 | 61 | 53 | 90 | 91 | 80 | 64 | |
| | 20 | 19 | 21 | 53 | 43 | 67 | 58 | 94 | 92 | 81 | 65 | |
| 4000 | 19 | 19 | 22 | 57 | 45 | 68 | 58 | 99 | 100 | 87 | 68 | |
| | 20 | 21 | 23 | 61 | 47 | 72 | 62 | 102 | 103 | 92 | 72 | |
| 3800 | 20 | 21 | 24 | 65 | 50 | 76 | 64 | 107 | 109 | 96 | 76 | |
| | 22 | 21 | 26 | 68 | 56 | 83 | 70 | 109 | 110 | 95 | 76 | |
| 3600 | 22 | 24 | 26 | 91 | 60 | 90 | 73 | 113 | 118 | 106 | 84 | |
| | 24 | 25 | 30 | 109 | 72 | 110 | 86 | 124 | 124 | 111 | 86 | |
| 3400 | 26 | 25 | 32 | 94 | 141 | 480 | 395 | 173 | 140 | 115 | 94 | |
| | 27 | 27 | 34 | 89 | 182 | 201 | 116 | 265 | 172 | 120 | 93 | |
| 3200 | 27 | 28 | 32 | 92 | — | 93 | 85 | 136 | 174 | 131 | 102 | |
| | 29 | 29 | 34 | 97 | — | 87 | — | 120 | 147 | — | 106 | 3144 = 232° C. |
| 3000 | 31 | 30 | 35 | 104 | 77 | 94 | — | — | 144 | — | 113 | Freezing-point of *tin.* |
| | 31 | 32 | 40 | — | 73 | — | — | — | 147 | — | — | |
| 2800 | 34 | 34 | 40 | — | 76 | — | — | — | 156 | — | — | |
| | — | 35 | 42 | — | — | — | — | — | — | — | — | |
| 2600 | — | 37 | 44 | — | — | — | — | — | — | — | — | |
| | — | 42 | 49 | — | — | — | — | — | — | — | — | |
| 2400 | — | — | 50 | — | — | — | — | — | — | — | — | |
| | — | — | 53 | — | — | — | — | — | — | — | — | |
| 2200 | — | — | — | — | — | — | — | — | — | — | — | |

## DESCRIPTION OF PHOTOMICROGRAPHS (PLATES 5–7).

### PLATE 5.

(FIGS. 12 AND 15 OMITTED.)

Fig. 8. The $\alpha$ phase with small quantity of eutectic in alloy 98. × 150.

,, 9. Decomposed $\beta$ phase in eutectic in alloy 95. × 1000.

,, 10. Typical structure of eutectic. Alloy 95. × 200.

,, 11. Typical structure of eutectic. Alloy 95. × 150.

,, 13. Hexagonal dendrite of $\beta$ phase ($Al_2Zn_3$). Alloy 95. × 200.

,, 14. Dendrites of $\beta$ crossing at angles near 60 degrees. Alloy 94. × 200.

,, 16. Alloy 90 cooled from fusion in 45 minutes. $\beta$ embedded in eutectic and partially decomposed at the edges. × 150.

,, 17. Alloy 86 cooled at the standard rate used for cooling-curves. $\beta$ almost completely decomposed. × 150.

,, 18. Alloy 86, under higher magnification, showing the laminated structure of decomposed $\beta$. × 500.

### PLATE 6.

Fig. 19. Alloy 80, slowly cooled after annealing at 430° C., showing the persistence of eutectic. × 150.

,, 20. Alloy 84, quickly cooled to a temperature just above 250° C. and then quenched, showing sheaths of $\beta$ surrounding primary $\gamma$. × 150.

,, 21. Alloy 84, slowly cooled from fusion, showing the more complete formation of $\beta$ and its subsequent partial decomposition. × 150.

,, 22. Alloy 84, annealed for a considerable time at 430° C. and then slowly cooled, showing the complete formation and decomposition of $\beta$. × 300.

,, 23. Alloy 84, annealed at 430° C. and then quenched from a temperature just above 250° C., showing the complete formation of $\beta$ and the prevention of decomposition by quenching. × 300.

,, 24. Alloy 78, slowly cooled, showing dark cores of primary $\gamma$ surrounded by sheaths of decomposed $\beta$ and a residue of eutectic. × 150.

,, 25. Alloy 78, similar to fig. 24, under higher magnification, showing laminated structure of decomposed $\beta$. × 500.

,, 26. Alloy 77, annealed at 430° C. and quenched just above 250° C., showing the homogeneous structure of $\beta$ or $\delta$. × 600.

,, 27. Alloy 77, annealed first at 430° C. and then just below 250° C. Laminated or pearlitic structure of decomposed $\beta$ or $\delta$. × 600.

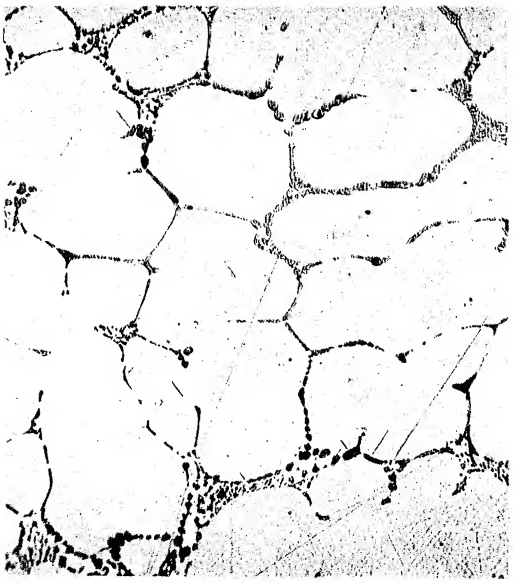

FIG. 8.

FIG. 9.

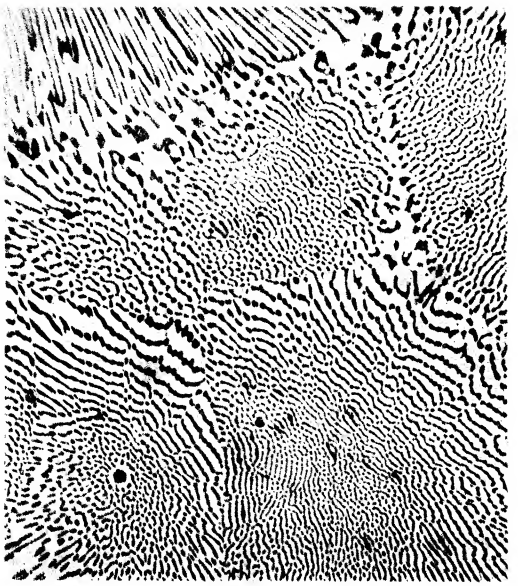

FIG. 10.

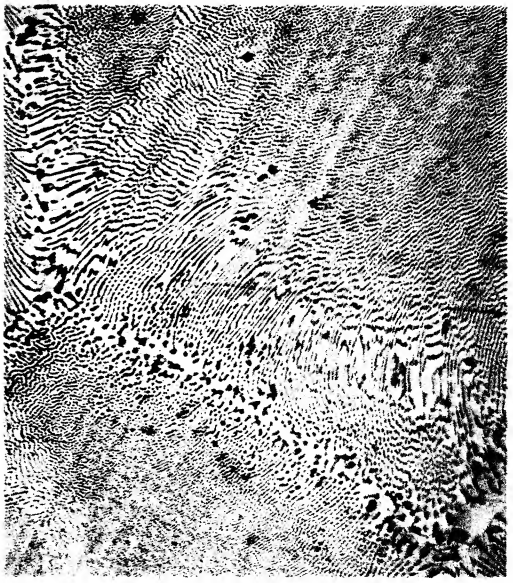

FIG. 11.

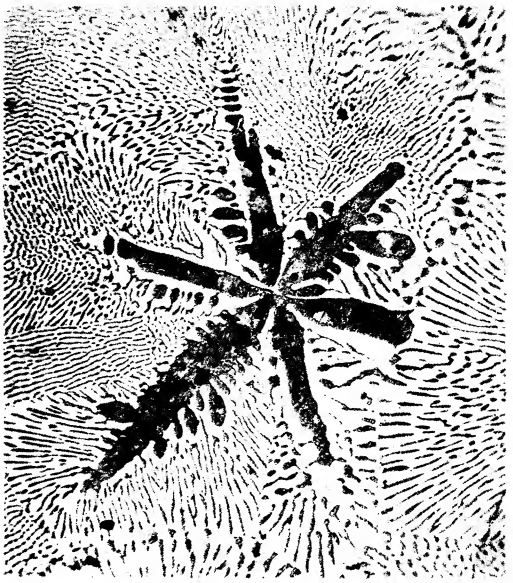

FIG. 13.

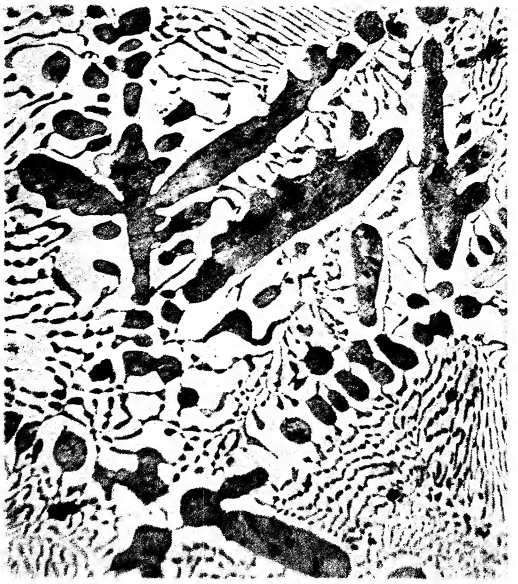

FIG. 14.

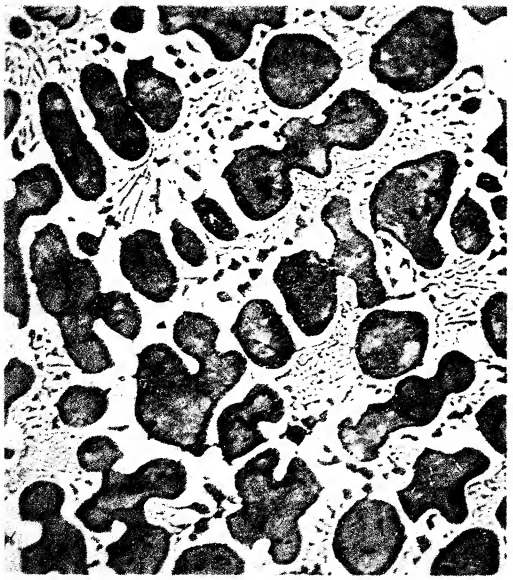

FIG. 16.

FIG. 17.

FIG. 18.

FIG. 19.

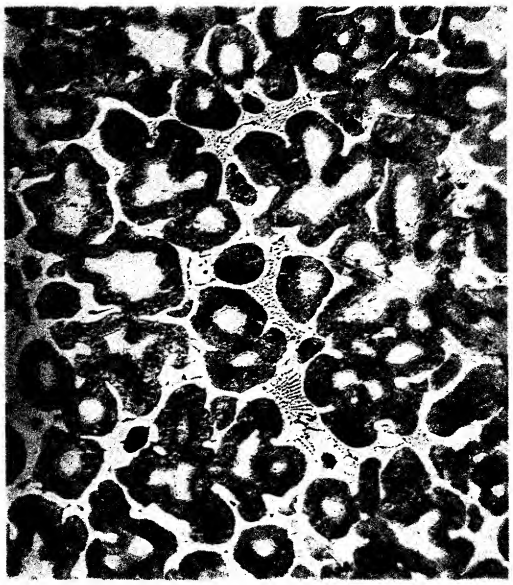

FIG. 20.

FIG. 21.

FIG. 22.

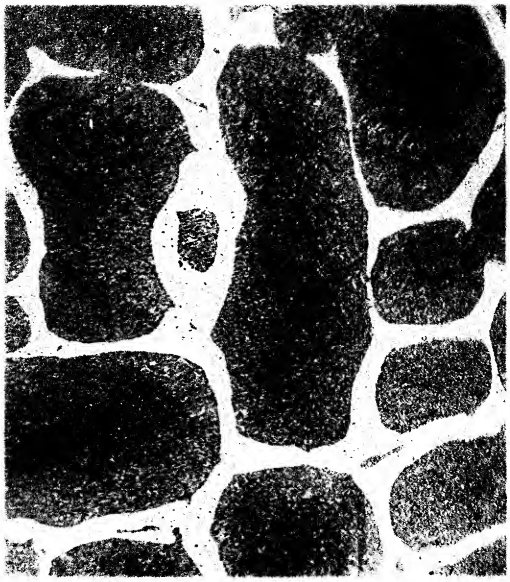

FIG 23.

FIG. 24.

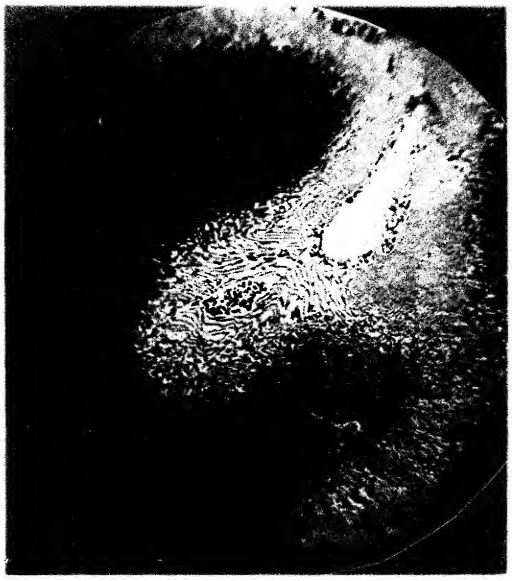

FIG. 25.

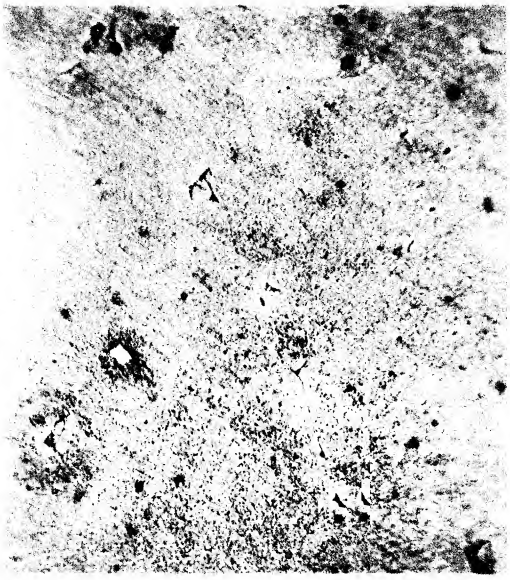

FIG. 26.

FIG. 27.

FIG. 28.

FIG. 29.

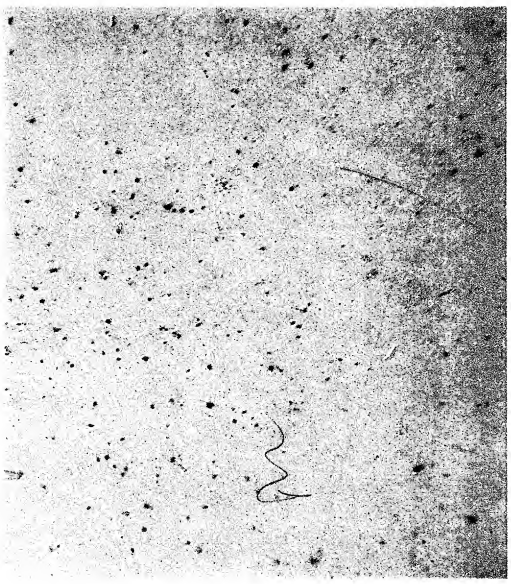

FIG. 30.

FIG. 31.

FIG. 32.

FIG. 33.

FIG 34.

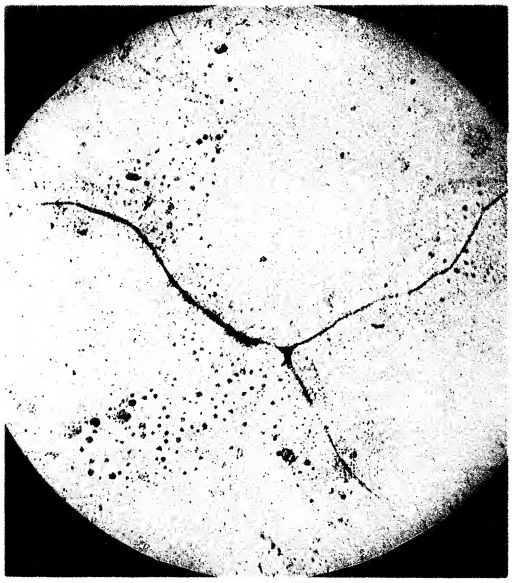

FIG. 35.

FIG. 36.

PLATE 7.

Fig. 28. Alloy 75, quenched from 470° C., showing $\gamma$ crystals surrounded by "liquid." Etched with nitric acid. × 150.

,, 29. Alloy 75, annealed for 30 minutes and quenched at 430° C., showing absence of "liquid" and approach to homogeneity. × 150.

,, 30. Alloy 75, annealed for 2 hours and then quenched at 430° C., showing homogeneous $\delta$. × 150.

,, 31. Alloy 75, annealed at 430° C., showing "pearlitic" structure of decomposed $\delta$. × 300.

,, 32. Alloy 70, slowly cooled, showing cores of $\gamma$, sheaths of partly decomposed $\beta$, and residues of eutectic. × 150.

,, 33. Alloy 70, slowly cooled after annealing at 430° C., showing "pearlitic" structure. × 170.

,, 34. Alloy 40, slowly cooled, showing cores. × 150.

,, 35. Alloy 50, quenched at 467° C., showing presence of "liquid." × 150.

,, 36. Similar alloy to fig. 35, quenched just above the solidus, showing slight traces of liquid. × 150.

FIG. 8.

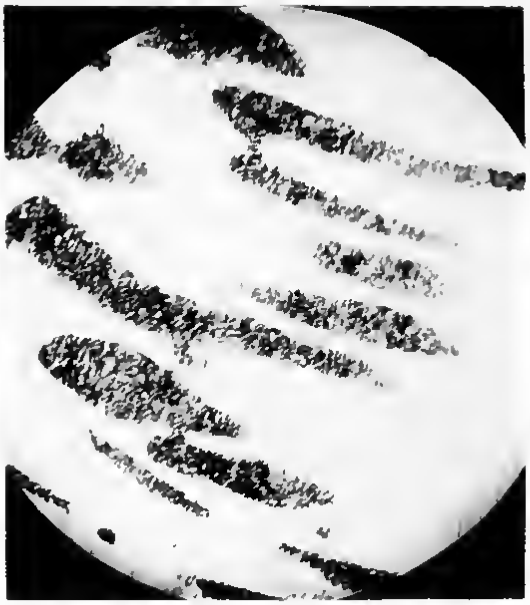

FIG. 9.

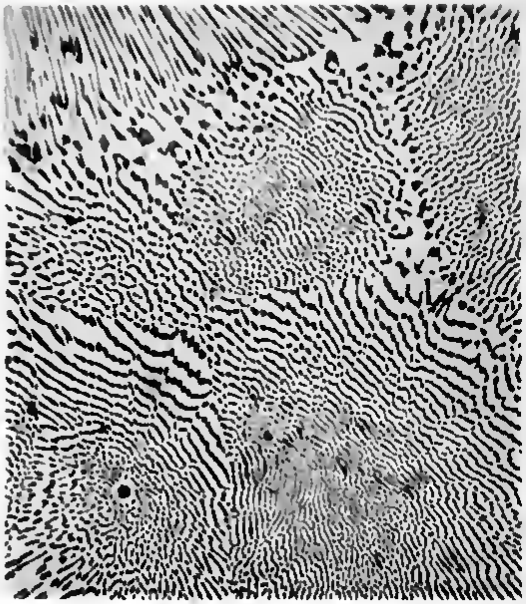

FIG. 10.

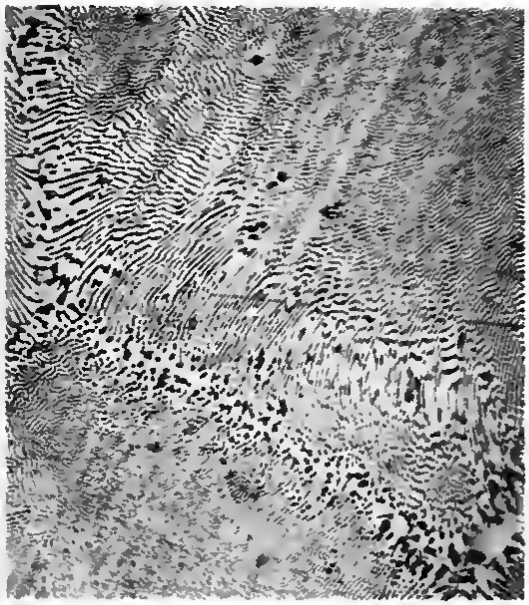

FIG. 11.

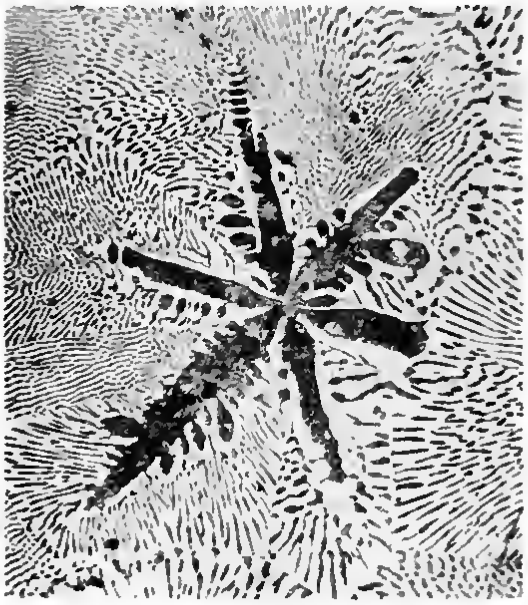

FIG. 13.

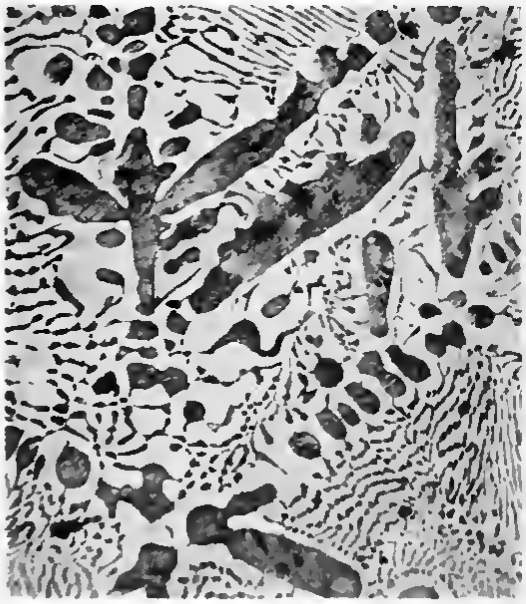

FIG. 14.

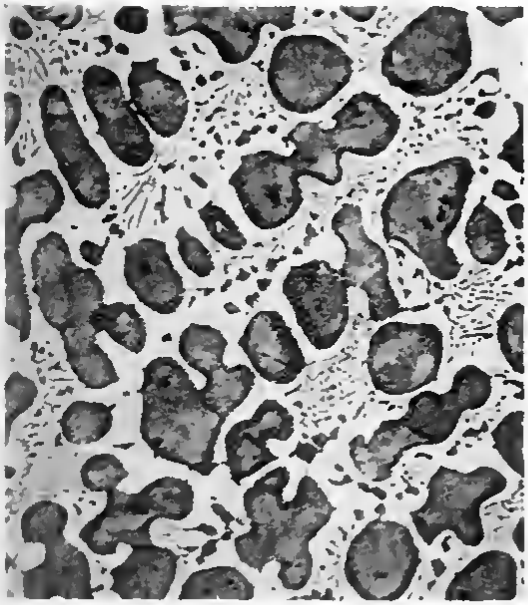

FIG. 16.

FIG. 17.

FIG. 18.

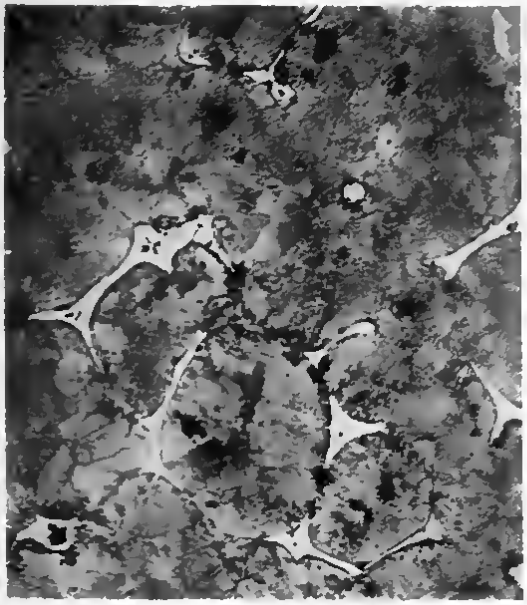

FIG. 19.

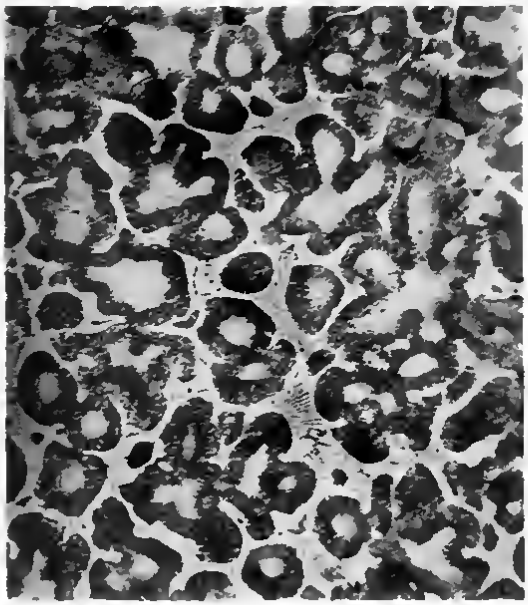

FIG. 20.

FIG. 21.

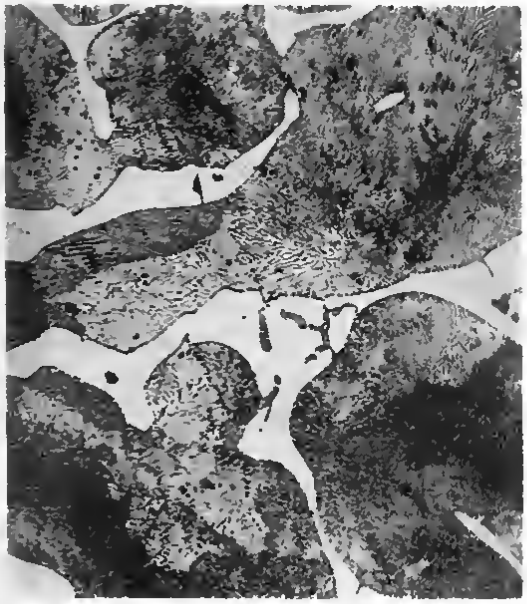

FIG. 22.

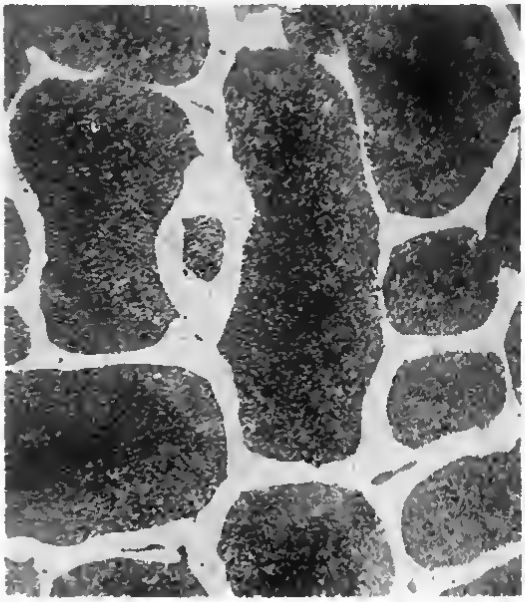

FIG 23.

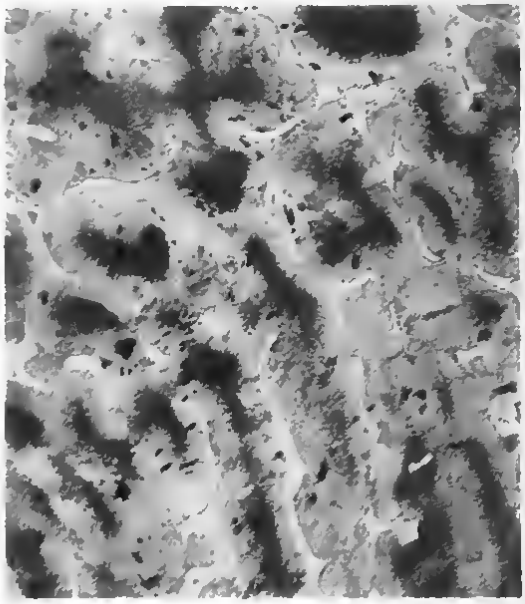

FIG. 24.

FIG. 25.

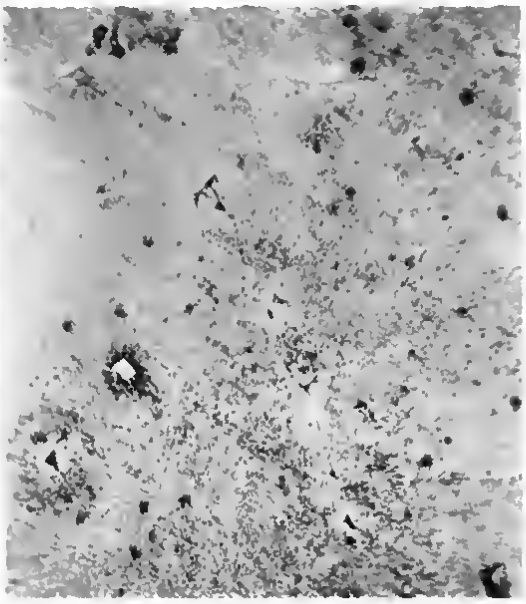

FIG. 26.

FIG. 27.

FIG. 28.

FIG. 29.

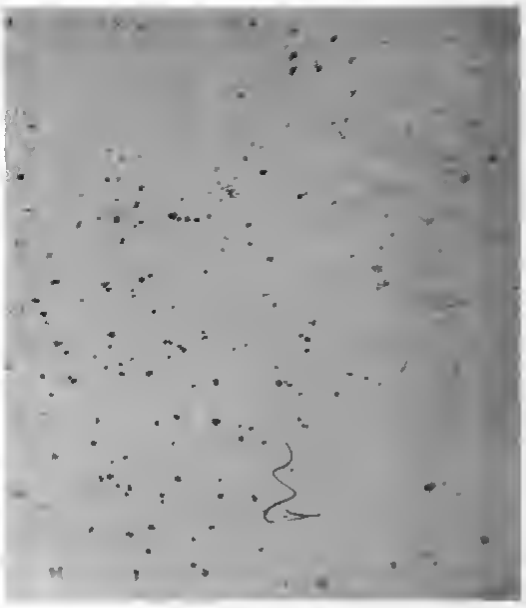

FIG. 30.

FIG. 31.

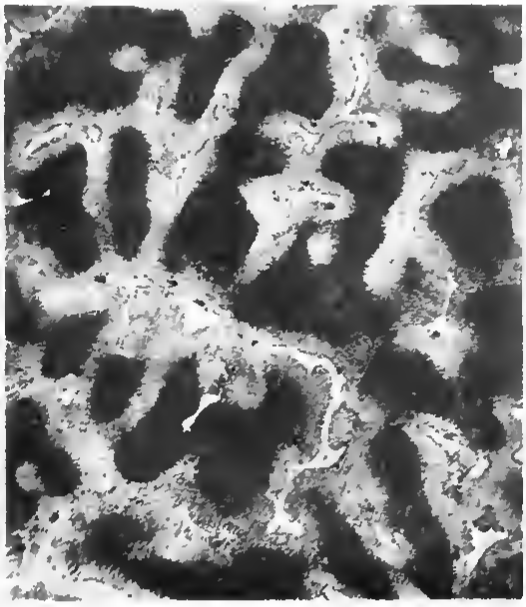

FIG. 32.

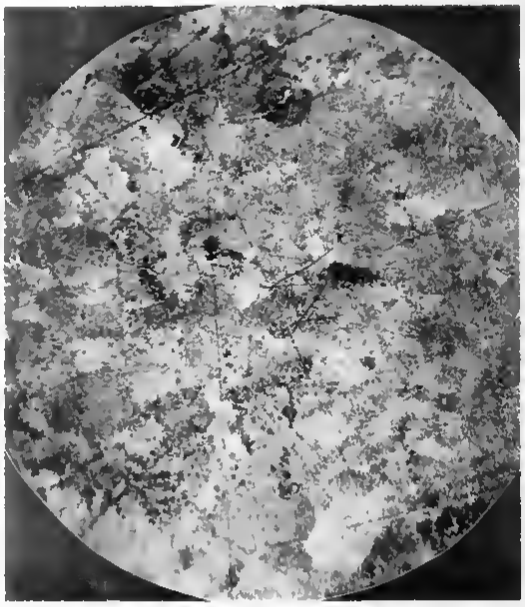

FIG 33.

FIG 34

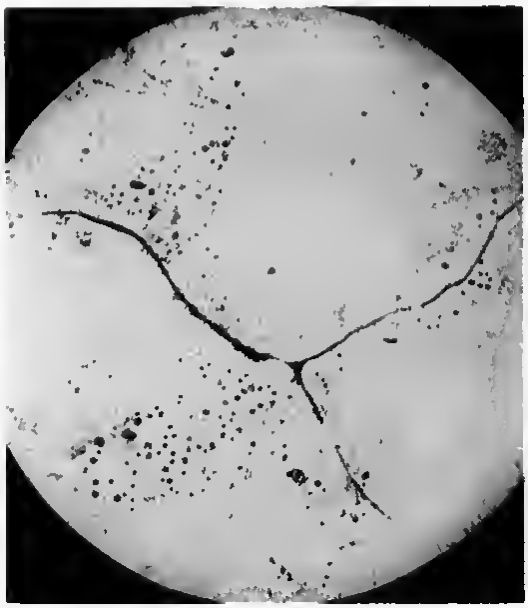

FIG. 35.

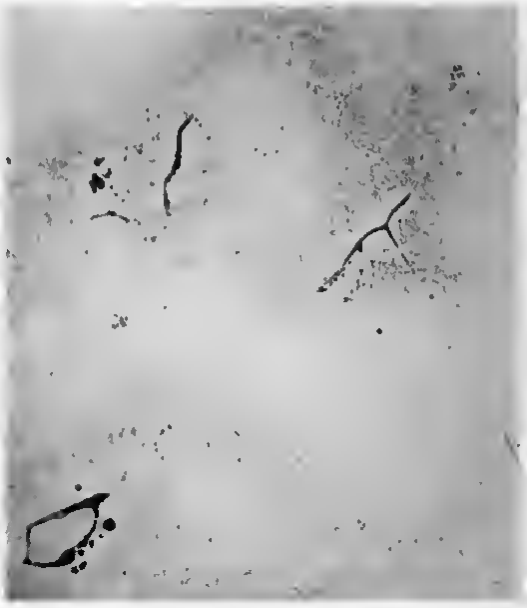

FIG. 36.